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FURTHER PROCESSING OF ANTIMONY CONCENTRATES

by

J. Dean Thibault, P. Eng.

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Copies available by contacting:

Mineral Resources
Department of Natural Resources and Energy
P.O. Box 6000, Fredericton
New Brunswick E3B 5H1

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ABSTRACT/RÉSUMÉ

Developments of pyrometallurgical and hydrometallurgical processing technologies for conversion of antimony sulphide concentrates to antimony trioxide and/or antimony metal have been extensively reviewed. Technical limitations of these add-on processes were identified and discussed in terms of their appropriateness to the Durham Resources Inc. antimony operation. A comparative assessment of the most promising technologies is presented and is based on both technical and economic factors. These include (1) Metal production by Induction Furnace, (2) Trioxide production by Rotary Kiln and (3) Trioxide production by Ferric Chloride Leach-Hydrolysis. As part of the assessment, a bench-scale laboratory program to test the effectiveness of the mentioned technologies on the Durham Resources Inc. concentrate was carried out in-house at DNRE's laboratory facilities. Special emphasis was placed on trioxide production by ferric chloride leach-hydrolysis as this technology demonstrated the greatest potential for an add-on processing plant. A conceptualized flowsheet was developed for a hydrometallurgical antimony products plant as a direct result of DNRE's laboratory investigation.

Les derniers développements en matière de procédés pyrométallurgiques et hydrométallurgiques en vue de la conversion de concentrés de sulfure d'antimoine en trioxide d'antimoine et/ou en métal ont fait l'objet d'une étude approfondie. Les limites techniques de ces procédés d'addition ont été cernées et examinées en fonction des besoins précis des installations d'extraction d'antimoine de la Durham Resources Inc. Une étude comparative des technologies les plus prometteuses a été effectuée du point de vue technique et économique. Parmi les procédés retenus on retrouve 1) la production de métal à l'aide d'un four à induction, 2) la production de trioxide d'antimoine à l'aide d'un four rotatif et 3) la production de trioxide d'antimoine à l'aide de la lixiviation/hydrolyse au chlorure ferrique. Dans le cadre de cette étude, on avait prévu un programme d'essais en laboratoire à petite échelle afin de vérifier l'efficacité des procédés en question sur le concentré de sulfure d'antimoine produit par la Durham Resources Inc. Ces tests ont été effectués dans les laboratoires du MRNÉ. On a porté une attention toute particulière au procédé de production de trioxide d'antimoine par lixiviation/hydrolyse au chlorure ferrique, puisque ce procédé semblait être le plus prometteur pour le genre d'installations de production visées. Un schéma de principe conceptualisé d'installations de production hydrométallurgique d'antimoine a été réalisé à partir des résultats des tests de laboratoire effectués par le MRNÉ.

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Editor's Note:

When this report was first assembled in March, 1986, the author was actively employed with DNRE. The original manuscript did not reach publication. All data presented in this edited version are unchanged from the original text.

1.0 INTRODUCTION

1.1 Objectives and Scope

The objective of this project was to review current commercial technology used in the production of antimony metal and/or trioxide from antimony sulphide concentrate.

A literature search was carried out to identify chemical processing concepts for treating antimony sulphide concentrate. Recommendations from publications by C.H. Kline and Co. Inc.[38] and Roskill Information Services Ltd.[37] provided useful input on marketing and growth expectations.

A bench scale laboratory study was designed and implemented at the Mineral Resources laboratory, D.N.R.E., to identify possible technical and economic limitations to an Antimony Products Plant (APP). Some processing options discussed in the literature indicated technical drawbacks which were characterized in the lab study.

This project will attempt to identify the most appropriate technology for use in treating antimony sulphide concentrate at Durham Resources Inc.'s concentrator. Also, areas for further research and study will be emphasized.

1.2 History of Antimony

The primary source of antimony is the mineral stibnite, Sb_2S_3, which was mined in China as early as 500 years ago. The extraction of antimony metal from ores has been carried out since the sixteenth century. Pyrometallurgical processes were generally adopted for metal production since hydrometallurgical methods were either unknown or uneconomical. Hydrometallurgy did not become significant until the late 19th and early 20th centuries, coincident to industrial expansion and advances in chemical knowledge and understanding.

The use of antimony metal in storage battery grids paralleled the growth of the automobile industry from the early to middle 20th century. Increased demand during the

1st and 2nd World Wars, where the metal was used as an alloy to harden lead, contributed to an expansion in Western Hemisphere smelting capacity. Following World War II, metal demand decreased but antimony trioxide gained prominence as a flame retardant.

Bolivia, China, South Africa and the Soviet Union are the world's major suppliers of antimony metal and trioxide today. Current data does not describe the degree of utilization of smelter capacity in North America.

1.3 Ores of Antimony

Antimony occurs primarily as stibnite, Sb_2S_3, and is carried mainly in quartz veins. Other antimony minerals which may be found in association with stibnite include: Berthierite, $FeSb_2S_4$; Polybasite, Ag_2SbS_6; Jamesonite, $Pb_2Sb_2S_3$; Livingstonite, $HgSb_4S_7$. Antimony oxide ores are rare and will not be described in this report.

Ores containing antimony are classified under the following headings:

(a) Auriferous: 40-70% antimony occurring as a sulphide with high gold content. If silver is present in economic quantity in addition to its gold, ores containing less than 40% antimony are classed as auriferous. Gold and silver are usually included in the Net Smelter Return (NSR).

(b) Antimony ores: 3-65% antimony. Mineralogically free from precious metals.

(c) Mixed Copper, Antimony and Zinc ores: Usually some lead and silver present.

(d) Lead/Antimony: 3-10% antimony with some silver present.

Although the exploitation of antimony ore deposits is limited due to mineralogical complexities with ensuing metallurgical difficulties, approximately 90% of new antimony production in the western world is from primary producers. The remaining 10% is as a by-product from base metal and gold processing operations.

1.4 Uses of Antimony

The principle use of antimony metal to date has been as an alloy with lead. Antimonial lead (up to 20% Sb) ensures grid tensile strength and the electrochemical stability of lead in wet cell batteries. The metal is also used as a hardener in bearing manufacture (it has the unique feature of expanding on being cooled and contracting slightly with heat). Ultra pure metal (99.99% Sb) is used as a dopant in n-type semiconductors such as indium, gallium and aluminum antimonites.

Antimony trioxide is used as a flame retardant and as an opacifier when added to plastics. Ultra fine trioxide sees some use as a tinting agent in the ceramics industry. In 1984, in the United States, consumption as a flame retardant accounted for about 38% of all antimony trioxide consumed. Table 1 lists other antimony compounds and their uses.

Table 1. Common Antimony Compounds

FORMULA	COMPOUND	FUNCTION	USE
Sb_2S_3	antimony sulphide	pigment	camouflage paint
$NaSbO_3$	sodium antimonate	fining agent	TV screens, fluorescent tubes
$SbCl_3$	antimony chloride	unknown	chemical
SbOCl	antimony oxychloride	unknown	chemical
Sb_2S_5	antimony penta sulphide	vulcanizing agent	rubber

The recent introduction of maintenance free calcium-lead batteries combined with used metal recycling has decreased the demand for primary produced antimony metal. At the

same time however, demand for antimony trioxide as a flame retardant has risen and is expected to maintain an annual growth rate of 3.6% in the United States.

1.5 Market Specifications

Antimony metal, or "regulus", must contain a minimum of 99.5% Sb and not more than 0.30% arsenic. Other limitations may be imposed depending on the buyers intended use.

Antimony trioxide is marketed either as a crude or finished trioxide. Almost all crude trioxide is reprocessed to a finished trioxide for consumption. Specifications for the final product are exacting and strict maximum amounts of arsenic, copper, lead, zinc, iron, nickel, selenium and mercury are enforced. Product sizing is also a critical factor in determining purity of finished antimony trioxide. A typical analysis of quality finished Sb_2O_3 is as follows:

Sb_2O_3		99.5% (as antimony trioxide)
Sb_2O_4		0.20% (as antimony tetroxide)
As_2O_3		0.11% (as arsenic trioxide)
PbO		0.15% (as lead oxide)
Fe_2O_3		0.03% (as iron oxide)
SnO_2		0.001% (as tin oxide)
S		0.18% (as sulphide)
Solubility in tartaric acid		99.5%
Solubility in water		0.4%
Whiteness measured by reflectometry		90.0%
Size distribution:	0-1.5um	60.0%
	1.5-3um	38.0%
	3um	2.0%
	44um	0.01%
Apparent density		0.8

Commercial grades of trioxide and metal are summarized in Tables 2 and 3.

Table 2. Commercial Grades of Antimony Trioxide

MANUFACTURER	TRADE NAME	Sb2O3*	As*	Pb*	PARTICLE SIZE,um
Anzon America	TMS	99.0	0.50	0.20	1.3
	Blue Star	99.5	0.10	0.10	N/A
	True Tint	99.0	0.50	0.20	1.3-2.3
	BFR-2	60.0	0.30	0.30	N/A
	A212	50.0	0.30	0.30	N/A
	Oncor 55	55.0	0.20	0.20	1.0-2.0
	Oncor 75RA	25.0	0.10	0.10	1.0-2.0
Asarco	Low Tint	99.5	0.02	0.20	1.8-2.2
	High Tint	99.5	0.02	0.20	0.9-1.4
	Very High Tint	99.5	0.02	0.20	0.7-0.9
Laurel Industries	Fire Shield L	99.3	0.50	0.07	2.5-3.5
	Fire Shield H	99.3	0.50	0.07	1.0-1.8
	Ultrafine II	99.3	0.50	0.07	0.25-0.50

* Percentage by weight

1.6 Processing of Antimony Ores

Antimony sulphide concentrates are generally produced by flotation of ores containing 5 to 20% Sb. Concentrate grades range from 50% to 65 % Sb with arsenic, lead and iron as contaminants. The grade of the concentrate dictates the processing method used in converting the sulphide to a marketable metal or oxide. Sulphide ores or concentrates that contain greater than 40% Sb are treated using direct reduction to avoid violent reactions at elevated temperatures. Producers of oxide and metal are identified in Table 4.

Table 3. Commercial Grades of Antimony Metal

Name of Brand *	U.S. Lone Star	Chinese	Japanese	Hungarian	Californian
Sb	99.7	99.760	99.195	98.27	98.34
Cu	-	0.012	0.043	0.54	0.021
Fe	-	0.004	0.007	0.63	0.144
Pb	-	0.029	0.424	-	0.410
As	0.05	0.090	0.095	-	1.008
Sn	-	-	0.012	-	-
Zn	-	0.027	0.023	-	-
S	-	0.078	0.201	-	0.06
Others	-	Co Nitrate	-	Bi 0.36	Co, Ni 0.013

* Percentage by weight

Pyrometallurgical processing of antimony sulphide concentrates has been classically adopted by industry for the conversion of stibnite to an oxide. The technology for producing a finished trioxide or metal using the hydrometallurgical approach is not yet available on a commercial scale. Companies consulted on available refining technology are listed in Table 5.

2.0 PYROMETALLURGICAL PROCESSING

Pyrometallurgical methods for the commercial production of antimony metal and/or antimony trioxide are currently being used in China, England, the United States and Bolivia. Antimony content of the feedstock is the predominant factor in determining the type of pyro process to employ as recovery technology is directly related to reactivity level. High temperature furnaces capable of processing a variety of feedstock grades are reported in the literature as follows:

Table 4. Major Producers of Primary Antimony Metal and Oxide in North America (1983)

COMPANY (LOCATION)	MAJOR PRODUCT	MAJOR FEED SOURCE	FEED GRADE	PROCESSING METHODS	ESTIMATED CAPACITY TONNES	PRODUCT USE
Anzon America (Laredo, Texas)	Sb* Sb_2O_3	South Africa South Africa	3-65%	N/A	10,000	Flame Retardants, Ceramics, Chemicals
Amspec (Gloucester City, NY)	Sb_2O_3	China Bolivia	N/A (Repackages Oxide)	Pyrometallurgical (Rotary Kiln)	N/A	Organo-metallics, Specialty Chemicals
Asarco (Omaha, Nebraska and El Paso)	Sb/Pb Alloy Sb_2O_3	Lead-Zinc-Silver Mine, Idaho Mine	N/A	N/A	3.000 (combined)	N/A
Chemet (Moscow, Tenn.)	Sb_2O_3 Sb*	N/A	N/A	N/A	N/A	Flame Retardants, Electronics
Laurel Industries (Texas)	Sb_2O_3	South Africa	N/A	Pyrometallurgical (Rotary Kiln)	10,000	Flame Retardants, Opacifiers
McGean Rohco (Columbus, Ohio)	Sb_2O_3 $NaSbO_3$	N/A	N/A	N/A	3,000 (combined)	Antimony Chemicals, Ceramics, Flame Retardants
M&T Chemicals (Baltimore)	Sb_2O_3 $NaSbO_3$	N/A	N/A	N/A	3,000 (combined)	Flame Retardants, Specialty Glasses
Sunshine Mining (Kellogg, Idaho)	Sb*	Copper-Silver-Antimony Sulphide Ore, Idaho Mine	N/A	Hydrometallurgical (Sodium Sulphide/ electrowin)	N/A	Granular Metal
U.S. Antimony Corp. (Thompson Falls,	Sb* Sb_2O_3	Thompson Mine	N/A	N/A	N/A	Flame Retardants

Table 5. Companies Consulted for Refining of Antimony

Company	Location	Background
Bepex Co-operation	Minneapolis, Mn.	Oxidation, roasting, calcination equipment suppliers and development of processing flowsheets.
Tolltreck	United Kingdom	Rotary kiln and reverbatory furnace design for antimony processing.
Campine, S.A.	Metacamp, Brussels	Producers of antimony regulus and refined products of antimony, offer no assistance in design.
Mannesmann Demag	Germany	Design of furnace flowsheets and equipment manufacturer.
Krupp Polusisus	Paris, France	Equipment supplier for rotary kilns, no process available for antimony refining.
Procedyne	New Jersey, USA	Development of flowsheet and equipment suppliers in fluidized bed technology.
Outokumpo	Mississauga, ONT	Offers no technology in antimony processing, have experience with pyro operations and design.
Lurgi	Montreal, PQ	Design of furnaces, no process available for antimony refining.
Sherritt Gorden	Saskatoon, SASK	Available for consulting on hydromet/ammonia and pressure sulfuric leach systems.
U.S.B.M.	Alaska/Nevada	Have done some work in the past on fluidized beds, sodium sulphide leaching and ferric chloride leaching; however, not specifically for Sb refining.
Canmet	Ottawa, ONT	Have done work with pyro development and ferric chloride leaching, not specifically for Sb refining.
R.P.C.	Fredericton, NB	Have done work with fluidized bed on Sb concentrates.
Chemet	Tennessee, USA	Available for consulting only.
Battelle Institute		Have done work with fluidized beds and sodium sulfide leaching, available for consulting and test work.
Occidental	California, USA	Hydrometallurgical hydrolysis and leach development using ammonia sulphide on stibnite.
Humbolt Wedag	Montreal, PQ	Design and operation of cyclone smelting for antimony refining.
Prochem	Mississauga, ON	Development of nitric acid leach, not specifically for stibnite.
Bechtel Ltd.	Montreal, PQ	Furnace manufacturers, no process available.

5-25% Sb: ores are volatilized (oxidation)

25-40% Sb: ores are smelted in blast furnaces (oxidation-reduction)

40-60% Sb: concentrates are liquated or iron precipitated (reduction)

The oxidation kinetics of stibnite are quite complex. The reaction is very exothermic and proceeds energetically, as reported by C.Y. Wang [10], starting at 340°C and may be terminating at 520°C. Due to its rapidity, the reaction may be very difficult to control and can result in undesirable reactions between the oxide and trisulphide. For antimony rich ores, therefore, reducing conditions are required.

The formation of antimony oxysulphides or "antimony glass" results from the fusing of trioxide and trisulphide in an uncontrolled reaction. Glass formation may cause fritting which limits sulphide conversion by blocking oxidation throughout the mass. Although the formation of antimony glass has not been extensively studied, it is known [9] to be a function of temperature and stibnite molar concentration.

The freezing point curve of a binary Sb_2S_3-Sb_2O_3 system is illustrated in Figure 1. As can be seen, oxypenta-sulphide forms at less than 550°C with high stibnite values. A glassy mass is produced on cooling.

It is apparent from the foregoing that process control parameters such as temperature, air volume, air quality and reagent additions are critical to the design of pyrometallurgical operating systems.

2.1 Oxidation

Antimony tetroxide, Sb_2O_4, and antimony trioxide, Sb_2O_3, are the two main products of oxidation. The process, quite volatile with respect to trioxide production, is referred to as volatilization roasting. It generally proceeds at around 500°C with trioxide formation occurring above 350°C according to the reaction

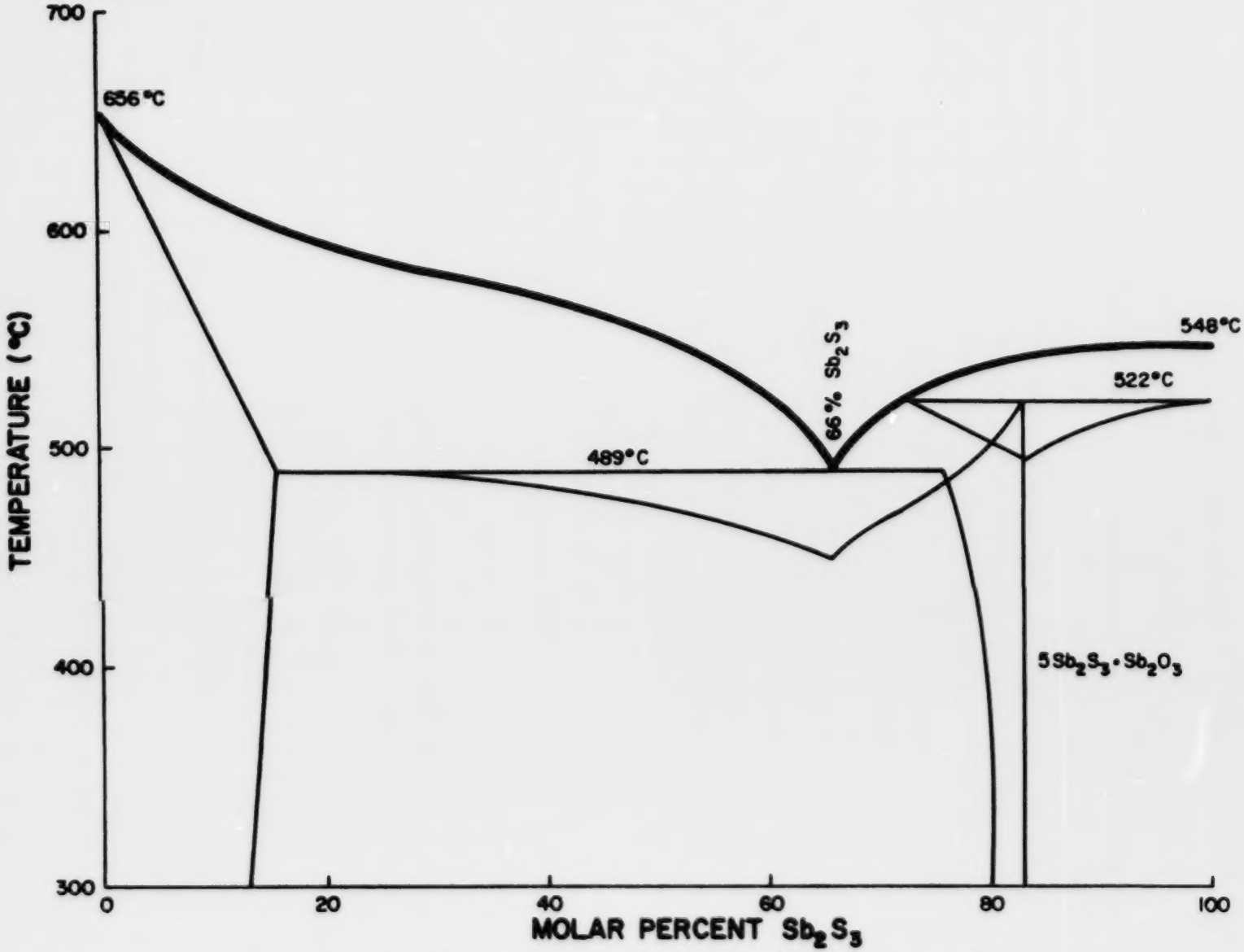


Figure 1. Phase Equilibria of Antimony Sulphide Oxide Complexes.

$$Sb_2S_3 + 9O_2 = Sb_2O_3 + 3SO_2.$$

Chemical changes during antimony oxide production are rather complicated. T. Carnelly and J. Walker [9] suggest that trioxide is stable in air up to 360°C and absorbs oxygen within a temperature range of 360°C to 400°C, thus converting to a compound containing Sb_5O_8. At around 750°C, as shown in Figure 2, tetroxide is the primary constituent. H. Baubigny [9] states that tetroxide is altered (Figure 2) to the trioxide state at around 1000°C.

Volatilization roasting for trioxide production is usually accomplished by limiting air to stoichiometric amounts and controlling temperatures around 500°C. Problems may occur, however, unless roasting is done on ores that contain about 15-25% Sb. Ores above 40% Sb have been known to partly volatilize and partly liquate. The liquated product, containing predominately molten antimony sulphide, combines with antimony oxide fume to form antimony glass. In addition, it has been found that most roasting furnaces develop "hot zones" that result in the fusion of silicate and antimony minerals which interferes with the operation of the furnace.

Additional problems may be due to the presence of excess moisture in either the feedstock or the air feed to the furnace. Water gas at a high temperature can affect the formation of trioxide with the simultaneous evolution of hydrogen sulphide (H_2S) gas. At about 550°C sulphide particles may take up moisture and form a hydrated sulphide complex which is red in colour, thus causing a reddish tint to occur in the trioxide fume.

Some advantages to using oxidation processing are summarized as follows:

(1) Arsenic, which is a common contaminate in most ores and concentrates, can be separated from antimony due to the fact that arsenic oxide is more volatile than antimony oxide. Arsenic will oxidize around 300°C and therefore can be selectively separated from antimony by temperature control. Oxidation temperature control is not commonly used, rather, arsenic is recovered by controlling cooling temperatures for selective sublimation of arsenic trioxide.

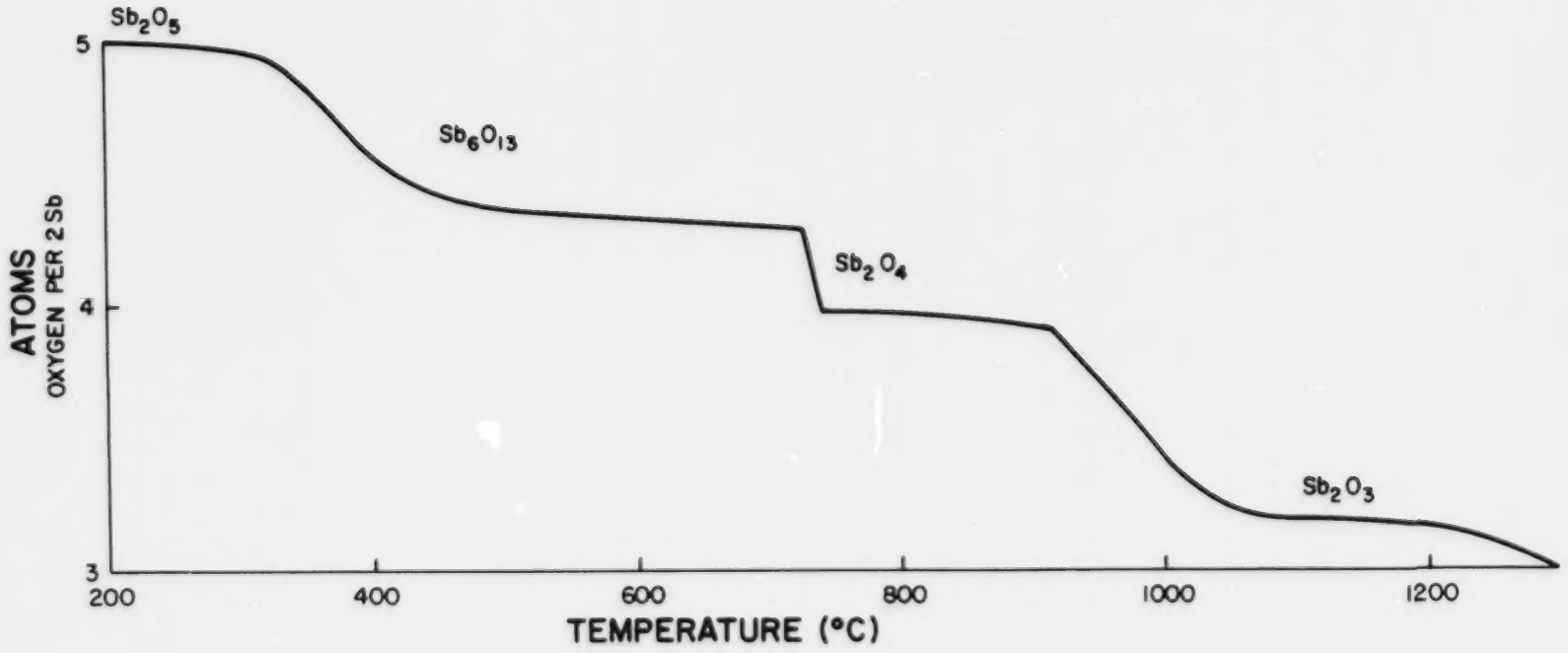


Figure 2. Stability of Antimony Oxide Compounds at Various Temperatures (Ref. 9).

(2) Contained gold or silver reports in the residue or slag after volatilization. The oxidation process usually renders the precious metals recoverable by conventional cyanidation technology although they may have been characterized as refractory in the feedstock.

(3) It is technically feasible to treat low grade ores because oxidation is not as rapid as it is with high grade concentrates.

(4) High recoveries of antimony trioxide are achieved by sublimation of the off gas stream and the use of high temperature gas filtration systems.

(5) Heat generated from the reaction may be used to operate the furnace at or near an autogenous heat demand.

(6) Antimony trioxide can be chemically reduced to metallic antimony by additional unit operations.

It is evident from the chemistry of oxidation that the design of a furnace to produce pure trioxide at high recovery will require a thorough knowledge of reaction thermodynamics and solids handling. I. Imris et al[5]. and O. Olija and I. Ilic[2] have bench tested and theoretically calculated the possibilities of pyrometallurgical treatment of concentrates (64 % to 68% Sb) by oxidation up to 700°C. The data address separating mercury and arsenic from tail gas as well as the effects of oxygen and temperature on product purity. The following observations made from these papers should assist in oxidation systems' selection.

(1) The oxidation of stibnite in the temperature range 337-545°C for a period of 3-5 hours results in a mixture of tri, tetra and penta oxides. The temperature at which stibnite is completely oxidized is around 548°C (see Figure 3).

(2) The reduction of Sb_2O_4 and Sb_2O_5 can be achieved by heating the oxides in combination with the addition of carbon monoxide. Ideal conditions for CO_2 were not tested but the following equations describe the reactions:

$$Sb_2O_5 + 2CO = Sb_2O_3 + 2CO_2$$
$$Sb_2O_4 + CO = Sb_2O_3 + CO_2$$

(3) Antimony recovery in the decomposition of tetrahedrite (copper-antimony sulphide) at 600-700°C is highest in a 1% oxygen environment. Figure 4 illustrates a decrease in recovery and an increase in calcine antimony content as oxygen concentration is increased. Neither the chemical composition of the calcine antimony nor the incidence of antimony glass formation is reported in the reference.

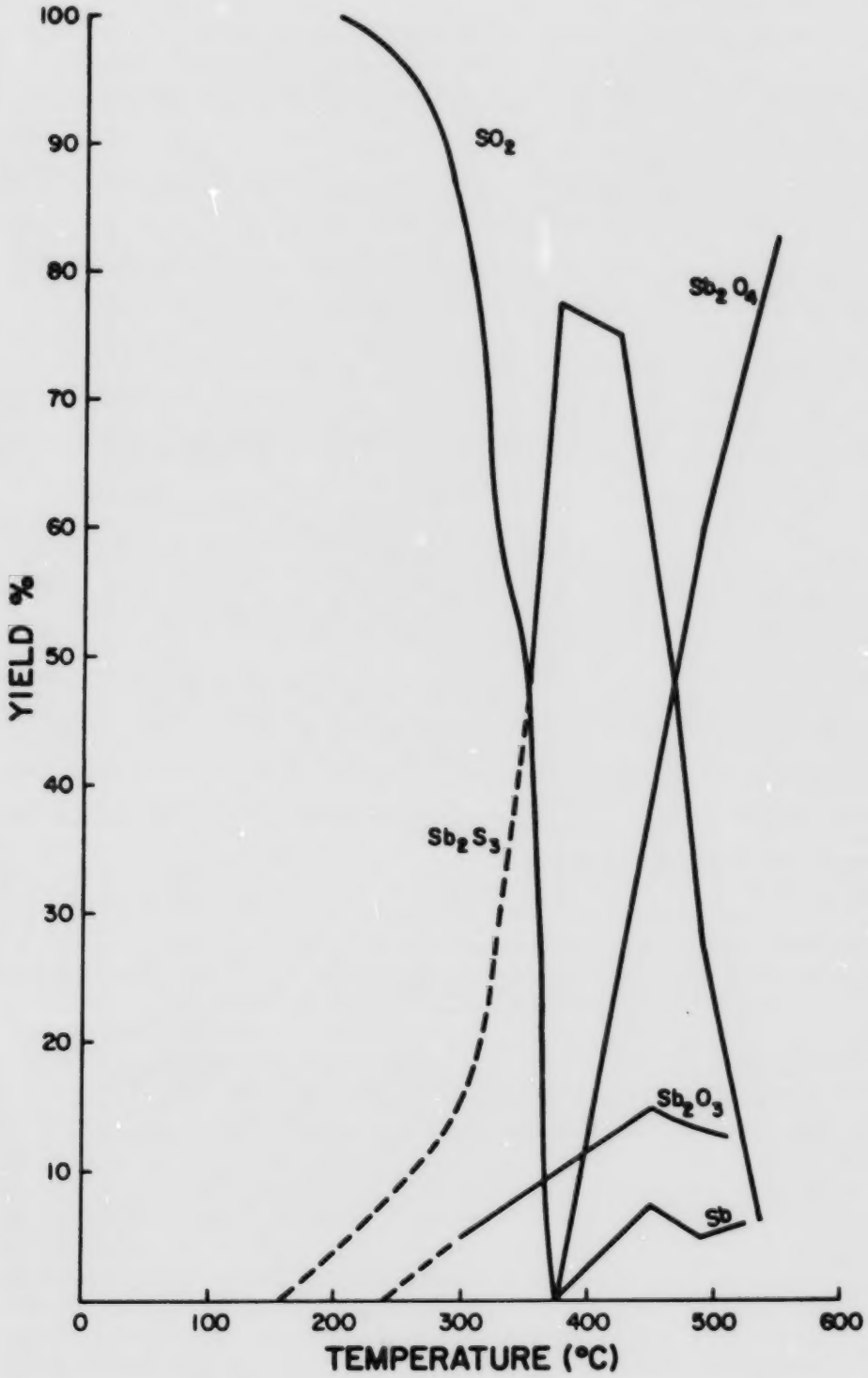


Figure 3. Yield of Oxidation Products as a Function of Temperatures (Ref 2).

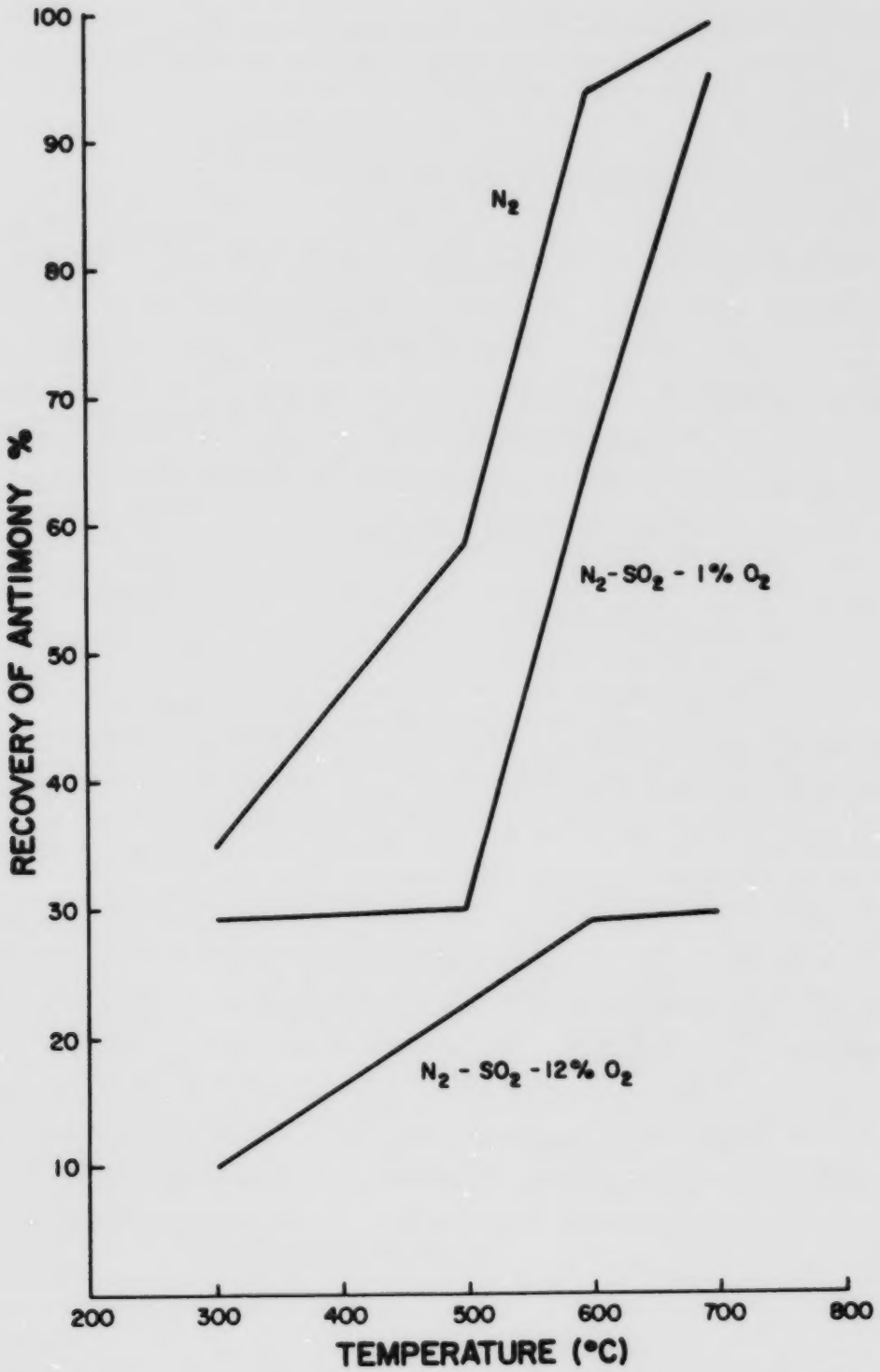


Figure 4. Recovery of Antimony in Tail Gas a Function of Oxygen Concentration and Temperature (Ref. 2).

(4) The formation of trioxide from other oxides occurs at temperatures above 1000°C. The effect of oxygen partial pressure on trioxide formation between 500°C and 2000°C has not been determined.

2.1.1 Volatilization Roast and Dead Roasting

Various types of furnaces were operated at the beginning of the 20th century for volatilization and dead roasting. Roasting temperatures were about 500°C and the yield of oxide was about 90% of the antimony contained in the ore. A charge of 6% charcoal was used in these furnaces for which maximum grades of ore did not exceed 20% Sb. There is no indication of the purity of the oxide produced from the early furnace operations in China and Yugoslavia (1906-1916). The major purpose of the volatilization roast was to upgrade ores for further refinement of antimony.

2.1.2 Rotary Kiln Application

The use of rotary kiln technology on antimony ores and concentrates was established around 1922 and has been commercialized in South Africa and South America for some time using a flowsheet similar to that in Figure 5. Details on plant design and operating procedures are regarded as being confidential and little information has therefore been printed on rotary kiln oxidation of stibnite.

It is known that high temperature in an oxygen poor environment results in 93% to 96% antimony recovery from high grade ores and concentrates. Also, rotary kiln operating conditions prevent the build-up of undesirable oxysulphides.

A drawback to rotary kiln operations is the delicate balancing of the generated heat of reaction to control operating temperatures at an optimum 1200°C. Calculations in Appendix II, Section E indicate that 21% of the heat required to maintain 1000°C is derived from the heat of reaction.

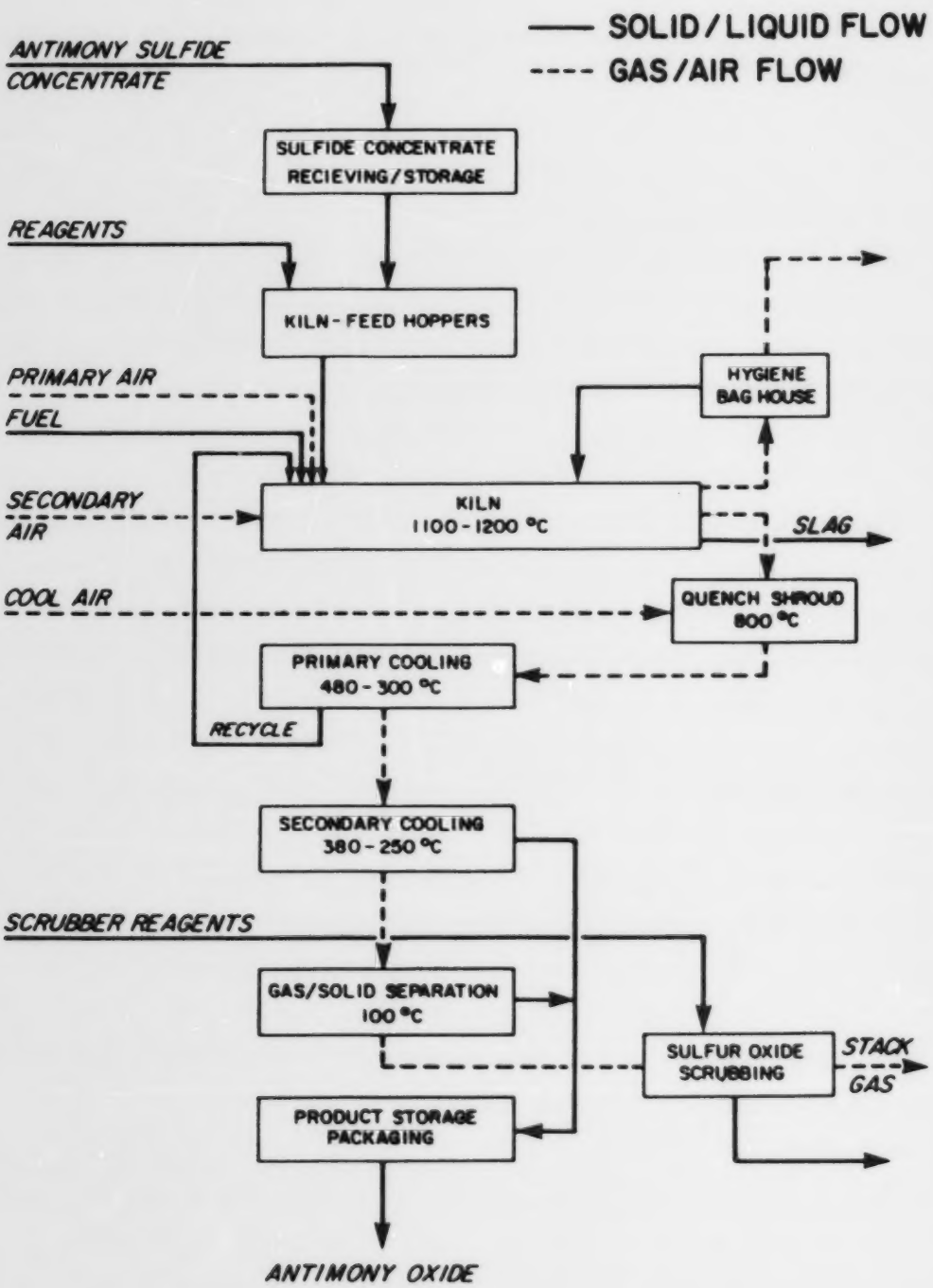


Figure 5. Process Flow Diagram for the Production of Crude Antimony Trioxide Using Rotary Kiln-Sublimination Technology.

In addition to the heat balance requirements, the rotary kiln method produces a crude oxide (95% Senarmontite) which must be subjected to further processing to make a finished product.

2.1.3 Fluidized Bed Technology

The technology for roasting antimony ores and concentrates in fluidized bed reactors is not yet fully developed. Tests were conducted by R. R. Wells (Alaska) et al[3] in 1958 and by P. D. Kunilov (Russia) et al[32] in the early 1970's in an attempt to solve the technology.

Wells wanted to extract mercury from a 34.6% antimony concentrate. He chose a fluidized bed reactor because he believed that the heat transfer between solid and gas in this medium lent itself to accurate temperature control, which was necessary for the extraction of mercury. Initially, attempts to maintain a fluidizing medium were unsuccessful because the volume of air required to fluidize the bed resulted in a highly exothermic reaction. Test runs at 520°C ended in the formation of antimony glass. Reportedly, fluidization was maintained using lower levels (around 3%) of oxygen.

Kunilov reported using fluidized bed technology on a feedstock of about 27% antimony. He found that the reactor could run autogenously at 480°C to 500°C with 1%-2% water in the feed. Oxide purity was not reported for either test.

The development of fluidized bed technology has economic merits as an add-on process to a concentrator for the following reasons:

(a) In a fluidized bed reactor, heat transfer between the particles and the fluidizing gas may prevent the formation of antimony glass by selective temperature control.

(b) Lower concentrate grade requirements should improve overall mineral recovery in the concentrator. It should be noted that roaster feedstock grade versus size of the roaster (where roaster size decreases with increases in feedstock grade) has to be established for optimum payback.

(c) If the reactor can be made to operate autogenously, excess heat can be used for auxiliary mine service. A slurried feed to the roaster would mean that a drying unit operation would not be required.

2.2 Reduction

As indicated previously, a reduction method is preferred for add-on processing of concentrates assaying 40-60% Sb. This is due to the high reactivity of the concentrate at these grades. In reduction processing, the objective is to reduce antimony oxide or antimony sulphide to metal. A reducing agent such as carbon or carbon monoxide is usually added to the feedstock as an oxygen scavenger. Potash or soda ash is added to the feed to form a fusible slag that, being lighter than the metal produced, floats on the metallic melt. Reduction of the sulphide occurs between 500-600°C according to the reaction:

$$Sb_2S_3 + 3Na_2CO_3 + 6C = 2Sb + 3Na_2S + 9CO$$

Antimony recovery by reduction may be limited by metal loss to slag and oxide loss in the off-gas.

2.2.1 English Precipitation Method

The English precipitation method (EPM) is used to refine high grade concentrates that do not contain appreciable amounts of arsenic and lead. The fundamental principle of the EPM is the reaction of iron with antimony sulphide concentrate to produce iron sulphide and antimony metal. Iron has a strong affinity for sulphur at 500°C according to the reaction:

$$Sb_2S_3 + 3Fe = 3FeS + 2Sb$$

The amount of iron used must be carefully controlled since excess iron will produce an iron-antimony sulphide which could cause product impurity and low metal recovery. Because iron sulphide has a high specific gravity, an alkali such as sodium carbonate is added which combines with the iron sulphide to form a fusible slag of low specific gravity. As antimony metal is formed it sinks below the slag due to its higher specific gravity. The

slag layer then prevents antimony oxidation. The English Precipitation method is also referred to as soda-precipitation.

Various studies[13,14] have shown that grade and recovery limitations using EPM may present serious drawbacks against the marketability of antimony metal because of metal purity. Studies using the different fluxing agents such as common salt (NaCl), soda ash (Na_2CO_3), sodium sulphate (Na_2SO_4) and limestone ($CaCO_3$) show average recoveries of 86.2% with a corresponding metal purity of 96.3%. The experimental data on these fluxing agents does not suggest that additional improvement in grade and recovery can be obtained. With an excess dosage of fluxing agents, the charge becomes very bulky and recovery drops. A healing interval (reaction time) of 0.75 to 1 hour was found sufficient for an optimum extraction. Data on recovery at various temperatures indicate the following relationships for the formation of antimony metal using iron oxide:

for 600 to 900°C, 50-75% recovery of Sb.
for 900 to 1100°C, 75-85% recovery of Sb.

The English precipitation method is usually carried out in a crucible furnace. Reverberatory furnaces are not used because of the high loss of antimony due to volatilization and slagging. Crucible material should be iron free to avoid degradation during the reaction.

Commercialized EPM processes have been reported by C. Y. Wang[10,11] but metal recoveries were not discussed. The product from a first melt is called "singles" and the product from a second melt is known as "star bowls". Conditions for each melt are reported for temperatures around 600°C for 2.5 hours and the amount of antimony loss due to volatilization is approximately 10%.

First Melt 42 lb ore, 16 lb iron, 4 lb salt, 1 lb slag from previous melt. Singles: 91.63% Sb, 7.33% Fe, 0.82%S, 0.32% insolubles

Second Melt 84 lb singles, 7-8 lb antimony sulphide, 4 lb salt. Star Bowls: 99.53% Sb, 0.18% Fe, 0.16 S

2.2.2 Hydrogen and Carbon Monoxide Systems

Reduction process technology using gas-solid systems is presently being developed on coal gasification products (carbon monoxide) and hydrogen gas systems. Product purity and metal recovery achievable from these processes are uncertain. This technology is not currently being used for commercial production of antimony products.

2.3 Combination of Oxidation-Reduction Processing

For the producer, the ability to produce both a metal (by reduction) and an oxide (by oxidation) would provide a competitive advantage with respect to long-term swings in market demand for either product. The major drawback to oxidation-reduction processing is the large capital investment required. There are two commercialized flowsheets for oxide and metal production which include the blast furnace and cyclone smelting concepts. These are illustrated in Figures 6, 7 and 8.

2.3.1 Blast Furnace - Chinese Production

The development of blast furnace methods to treat antimony sulphide feedstocks of 25-40% Sb was initiated in the early forties. The behaviour of stibnite was found to be different from other metallic sulphides in that a blast furnace can smelt unroasted stibnite ores.

For blast furnace operations, about 80% of the antimony in the feed is volatilized. The flowsheet (shown in Figure 7) of the blast furnace operation in Xikuangshan (China), developed in 1960, recycles the antimony matte and recovers the volatilized oxide through gas cooling units. The oxide is further reduced to produce an antimony ingot. Recovery of antimony fluctuates between 92% and 98% with metal grades of 97% to 98%. Blast furnace performance is strongly dependant on briquette quality and flux consumption as well as air volume. The blast furnace operates on relatively low pressures of air (3" Hg for 19' column).

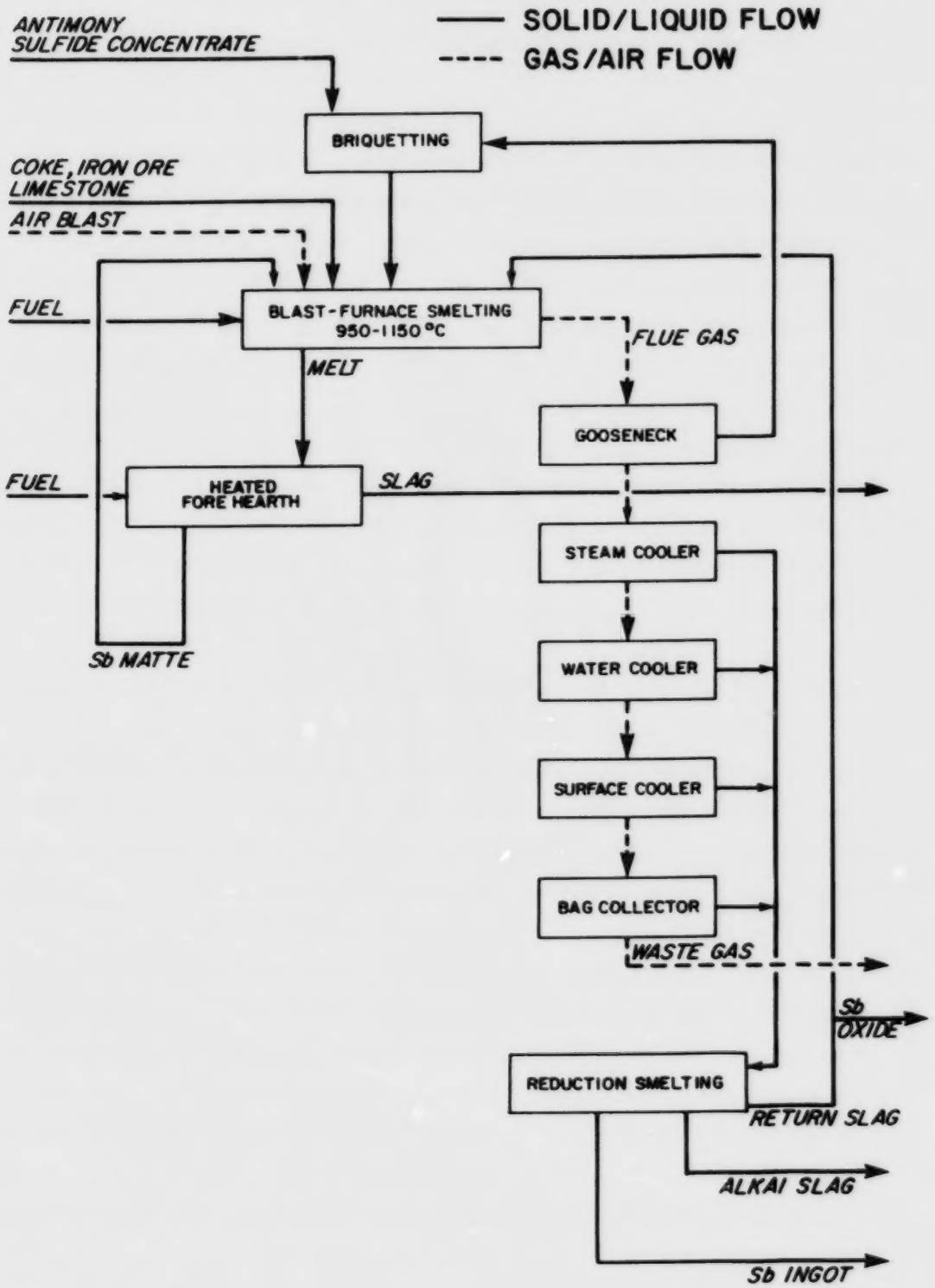


Figure 6. Process Flowsheet for Blast Furnace Smelting of Antimony and Gold Concentrates, Using a Reduction Smelter to Produce Metal From Oxide.

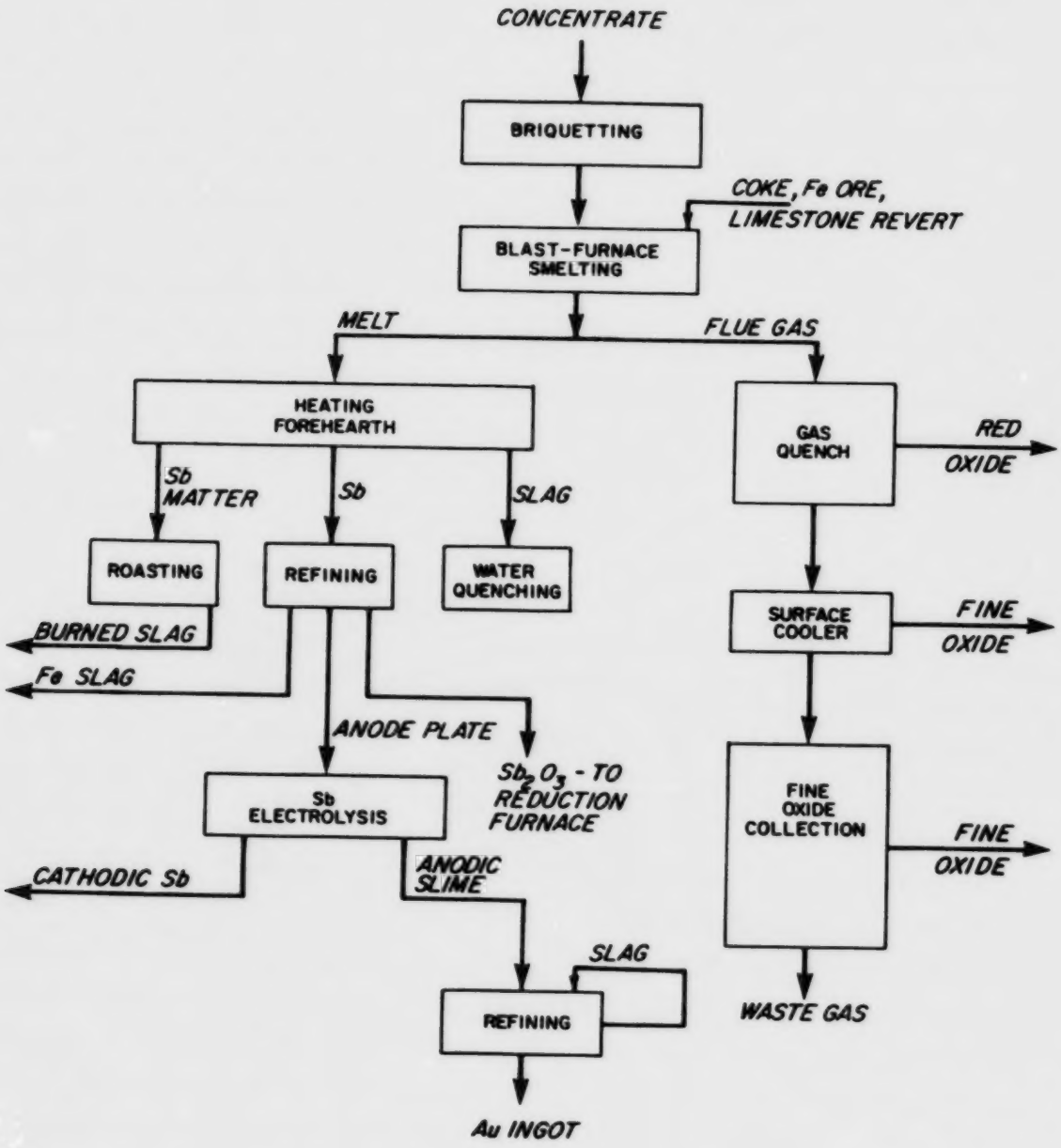


Figure 7. Process Flowsheet of Blast Furnace Operation in Xikungshan (China), Using Various Unit Operations to Produce Oxide, Metal, and Gold Ingots.

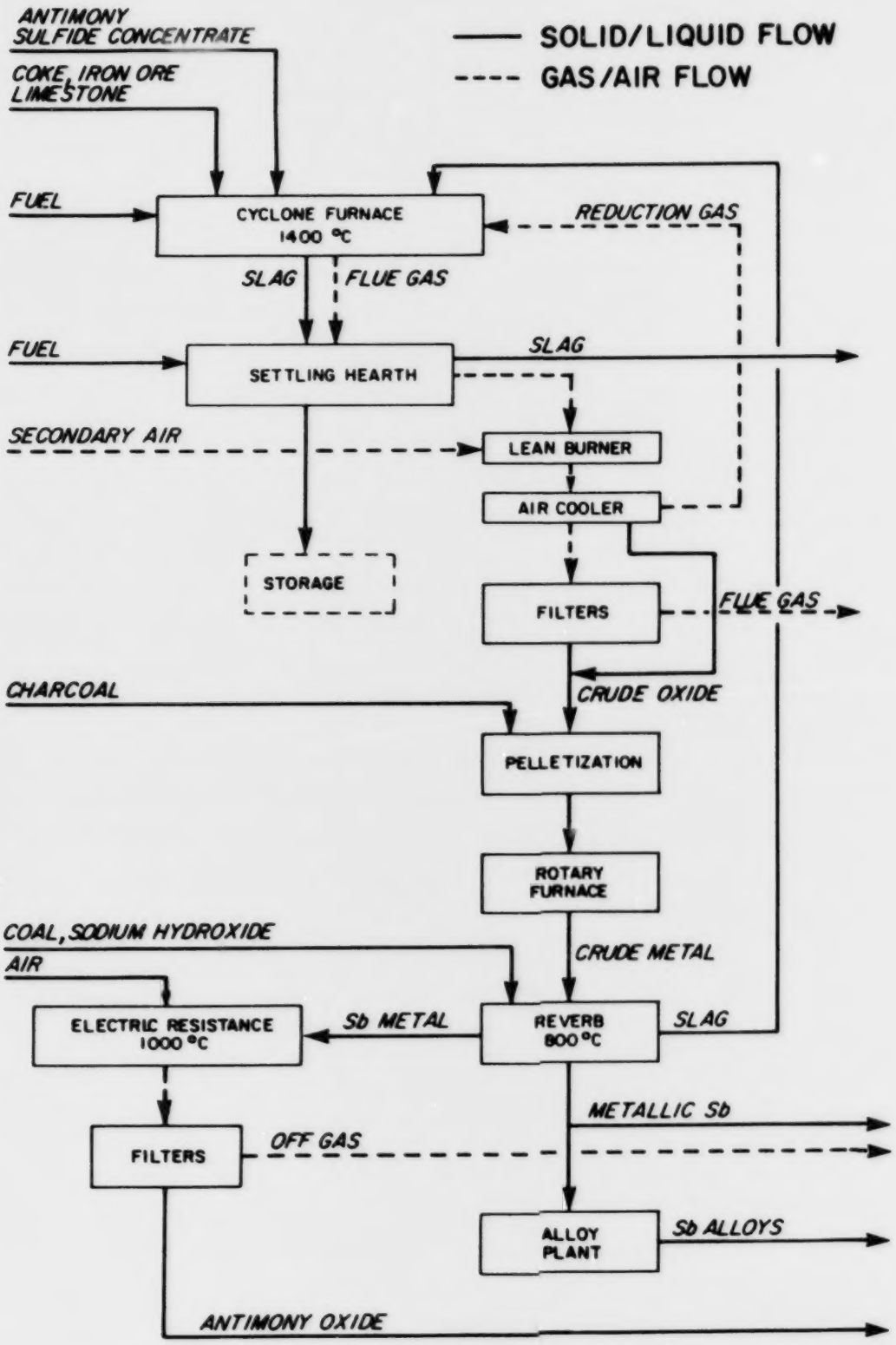


Figure 8. Process Flowsheet for Cyclone Smelting at Vinto (Bolivia) Using Various Oxidation-Reduction Unit Operations.

Heat utilization is very low in blast furnaces. This accounts for high coke consumption which is usually 20-25% of total charge. With feed grades of 25-40% Sb, the heat consumed in the direct sublimation of Sb_2S_3 has been reported to have a considerable cooling effect. The sublimation of the sulphide results from immediate contact of fresh feed with hot gases. The oxidation of sublimed sulphide occurs in the gooseneck of the furnace and results in excess levels of tetroxide and "red antimony oxide".

For the Chinese blast furnace flowsheet, there is no indication in the literature that additional processing is necessary to produce marketable antimony trioxide. The "red antimony oxide" (50-70% Sb) collected in the gooseneck has minor amounts of antimony sulphide and is recycled to the furnace. "Sintered antimony oxide" (75-78% Sb) is collected from the steam and water coolers and "fine sintered oxide" (78-81% Sb) is collected on the surface cooler. The "fine oxide" is collected in the baghouse (80-82% Sb).

2.3.2 Cyclone Smelting - Bolivian Production

The concept of cyclone smelting (see Figure 8) was designed by Skodaexport of Czechoslovakia. The first unit was installed in 1975 at Vinto, Bolivia. In order to avoid high consumption of coke and to maintain an operation compatible with high grade feedstocks (at least 60% Sb and less than 0.5% lead and arsenic), the cyclone smelting furnace was designed to operate under slightly reducing conditions with a gas content of 4% to 5% carbon monoxide. Excess amounts of coal are required to maintain reducing conditions at an operating temperature of 1400°C. Hot air recycle which controls the heat balance in the cyclone furnace, requires precision process control technology. In addition, particle size of the feed is very critical with respect to reaction kinetics. At the Vinto smelter[9], the feed is usually a blend of coarse gravity and flotation concentrates. Product metal grade reaches 99.6% Sb at 92% recovery.

Crude oxide is produced as a volatilization product from the cyclone furnace and is reduced in six rotary furnaces to produce a crude metal. Caustic soda and soda ash are used to refine the metal in three reverberatory furnaces. The slag from the reverb contains

about 4% Sb and is recycled to the cyclone furnace. Two small electric furnaces are used for producing high purity trioxide using refined metal as feed stock.

2.4 Volatilization-Chlorination Roasting

The chlorination process has not been used for commercial production of antimony products. However, the production of metal chlorides from other sulphide ores has been developed. The major drawback to the development of chloride systems is the corrosive environment of solutions and gases. In high-temperature chloride operations, metal chlorides and sulphur can be separated by controlling condensation temperatures. A hydrolysis process might then be used to produce trioxide from antimony chloride.

2.4.1 Gaseous Chloride System

Development of high temperature chlorination systems for processing antimony concentrates and ores was investigated by Occidental Petroleum Corporation (OPC) in the early seventies. A process for the production of high purity antimony chloride as shown in Figure 9 has been patented by OPC. Ore is chlorinated in a fluidized bed at 400-550°C and, by continuous distillation, antimony chloride (having a low boiling point of 220°C compared to other metal chlorides) is recovered. Overall recovery of sulphur has been reported at 95% with an antimony chloride purity of 99.9%. The process was developed to provide better control on product purity from feedstocks containing high levels of arsenic, iron and sulphur.

The advantages of high temperature chlorination (HTC) are, reportedly, lower capital costs compared to blast furnace technology. With HTC a high purity product is attained at much lower temperatures than that required by a blast furnace. However, a heat balance for the operation of a fluidized bed chlorinator has not been reported.

A major drawback to HTC is the cost of chlorine. As reported in the OPC patent, 9 parts by weight of Cl_2 is required for every 19 parts of concentrate (grade not reported).

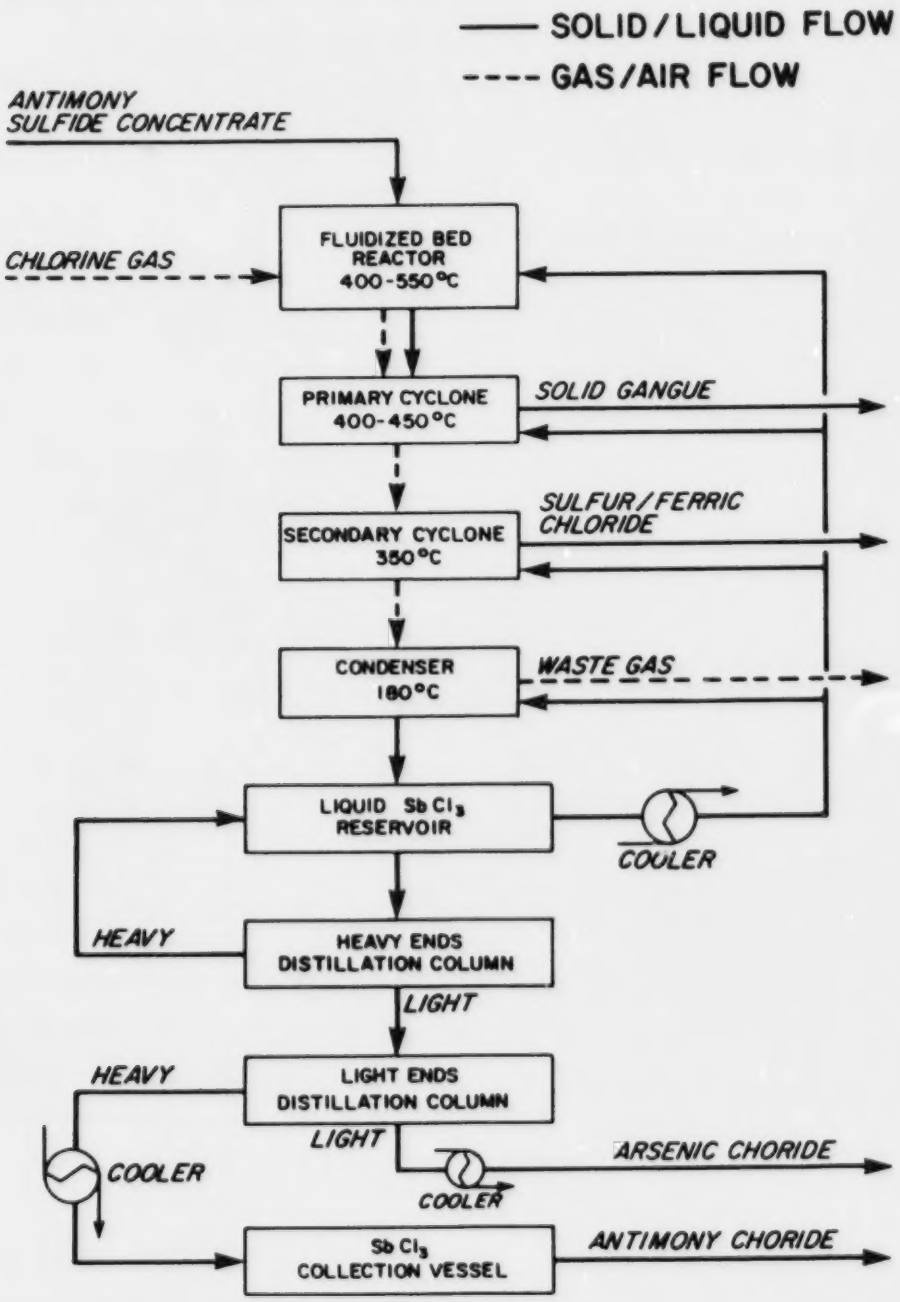


Figure 9. Process Flowsheet for Production of Antimony Chloride Using Temperature Chlorination, Occidental Petroleum Corp. Patent 1971. (Ref. 19)

This results in a reagent expense of about $305 per tonne of concentrate based on the cost of chlorine gas in New Brunswick. For the technology to be commercially viable, a method of regenerating chlorine would have to be developed.

2.4.2 Calcium Chloride Roast

Further development of HTC using recycle calcium chloride as illustrated in Figure 10 was done in 1980 by the Department of Mineralogy, Bureau de Recherches Géologiques et Miniéres (BRGM) (Orléans, France). It has been reported[24] that the rotary kiln roasting of stibnite in the presence of calcium chloride, sulphur dioxide, and oxygen at temperatures around 500°C results in the rapid oxidation of stibnite followed by oxide chlorination.

The overall reaction is

$$Sb_2S_3 + 3CaCl_2 + 6O_2 = 3SbCl_3 + 3CaSO_4$$

following the assumed reaction path of

$$Sb_2S_3 + 9/2O_2 = Sb_2O_3 + 3SO_2 \quad (a)$$
$$3CaCl_2 + 3/2O_2 = 3CaO + 3Cl_2 \quad (b)$$
$$Sb_2O_3 + 3Cl_2 = 2SbCl_3 + 3/2O_2 \quad (c)$$
$$3SO_2 + 3/2O_2 = 3SO_3 \quad (d)$$
$$3CaO + 3SO_3 = 3CaSO_4 \quad (e)$$

The chlorination of antimony sulphide is very attractive economically since calcium chloride can be regenerated and the roasting process is autothermal. The recycle of calcium chloride is achieved by the addition of calcium hydroxide to the resulting chloride solution after hydrolysis. By evaporation and crystallization, calcium chloride is regenerated.

Technical information is not available on calcium chloride roasting. Bench scale tests were conducted by BRGM on 45% Sb concentrate using a mass ratio of 0.45 concentrate and 0.55 calcium chloride (which represents 50% in excess of the stoichiometric requirements of calcium chloride). An oxide yield of 90% was reported. Recoveries were

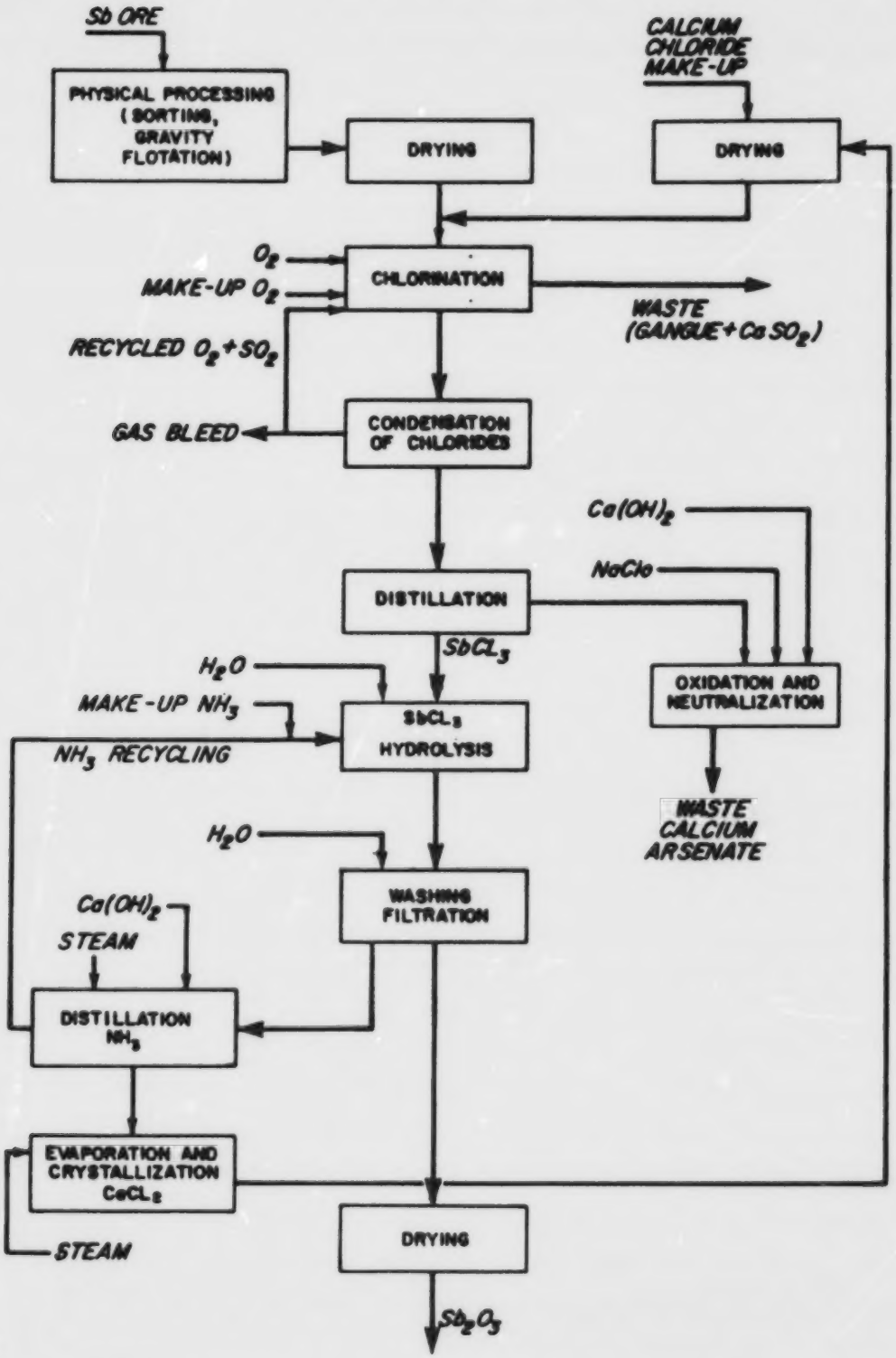


Figure 10. Process Flowsheet for Senarmontite (Sb_2O_3) Production Using High Temperature Chloride and Recycle of Chlorine as Calcium Chloride. (Ref 24)

not accounted. Impurities such as As and Pb were removed by distillation of the chlorinated roaster products.

2.5 Summary of Pyrometallurgical Processing

It has been difficult to assess pyrometallurgical processing limitations because of the small amount of information available concerning grade recovery relationships to operating parameters. The technologies developed to date have been summarized in Table 6. The identified limitations can be summarized as follows:

(a) The thermodynamics and reaction kinetics of antimony sulphide oxidation result in the uncontrollable formation of oxides. The chemical properties of stibnite dictate high heat for finished trioxide whereas waste heat circulation is critical for an economic heat balance.

(b) Antimony complexes result from antimony sulphide reacting with the oxide to form antimony oxysulphides. Antimony metal will complex with sodium and iron. The formation of these complexes results in low antimony recoveries.

(c) Impurities in the feedstocks, such as lead and arsenic, have chemical properties similar to antimony and are difficult to remove from the final product.

(d) Crystalline form of oxide is a major specification for the trioxide market. The literature does not elaborate on the technology of the cubic trioxide formation as a function of sublimation operating conditions. In addition to crystalline form, particle size control is critical to meeting marketing specifications.

(e) Sulphur dioxide emissions are difficult to reduce because of the large volume of air used in some furnaces for oxidation and the volume of air used to quench the waste gas for oxide sublimation will lower the sulphur dioxide concentration in the gas stream.

The primary reduction of sulphide ores (English precipitation method) has a significant recovery problem where the metal is very stable in slag. It appears that the optimum metal recovery method is primary oxidation of sulphide to produce an oxide and then reduce the oxide to a crude metal. Combining the oxidation and reduction unit operations is necessary in order to achieve marketable grades of trioxide and/or metal. The major drawback to this strategy is that each operation is very capital intensive.

Table 6. Summary of Pyrometallurgical Processing of Antimony Sulphide

Process Technology	State of Development	Process Limitations	Process Advantages
Volatization - Dead Roast (oxidation)	•commercialized since 1906 using reverberatory furnaces. Operations of dead roast are not common in North America and see limited use in Europe.	•fitting of mass results in low recoveries (around 90%). Close control of temperature is required around 500°C with high consumption of charcoal. •maximum grade of feed cannot exceed 20% Sb. •various oxides result in fume.	•enables upgrading of low grade material that cannot be beneficiated because of complex mineralogy.
Rotary Kiln Methods (oxidation)	•commercialized since 1922, used extenstively today by African and North American processors.	•requires down time for deslagging. •additional fuming required to produce high purity oxide. •heat of reaction provides 21% of overall heat requirements.	•operates at high temperatures to enhance the stability of trioxide formation. •mechanical agitation of slag overcomes glass formation with recoveries of oxide in the range of 93-96%. •able to handle high grade antimony concentrates.
Fluidized Bed (oxidation)	•bench-pilot scale development done extensively by Russians.	•will operate on low feed grade only where fluidization cannot be maintained due to fritting. •quality of product uncertain. •limitation on particle size of feedstock with respect to reactor design. •sulphur dioxide emission may be difficult to treat because of high gas volumes required for fluidization.	•may operate autothermal.
Precipation Method (reduction)	•previous to 1939, used commercially by the Chinese. Further development on reaction chemistry 1970's.	•feedstock must be free of arsenic and lead so that where high grade antimony can be treated. •high temperatures (1200°C) required to overcome high slag viscosities. •limited understanding of fluxing agent chemistry. •significant loss of antimony by volatization and entrapment is slag; recoveries of antimony around 80%.	•technology to produce Sb metal from sulphide. •low capital investments using pot furnaces. •limited sulphur emission where sulphur is complexed with iron in slag.

Table 6. Summary of Pyrometallurgical Processing of Antimony Sulphide

Process Technology	State of Development	Process Limitations	Process Advantages
English Blast Furnace (oxidation)	•commercially operated by the Chinese previous to 1939, modified from lead smelting practices.	•feedstocks are limited to 25-40% Sb. •about 80% of antimony in feedstock is volatilized and remainder is recycled after being deslagged. •high consumption of coke. •heat utilization limited. •feedstock requires pre-treatment. •high gas volume and low sulphur content limits flue gas treatment. •mixture of oxides in flue.	•recoveries reported between 92-98%.
Cyclone Smelting (reduction)	•commercially operated in Bolivia in 1975.	•restriction on particle size of feedstock. •recirculation of gas streams to achieve reducing conditions, and maintain heat balance, requires integrated process control.	•feedstock grade unlimited. •low consumptions of coke. •overall recoveries exceed 92%.
Fluidized Bed Chlorination	•bench scale development and technology for chlorination-distillation patented 1975.	•restriction on particle size. •corrosive environment at of elevated temperatures (500°C). •chlorine used as reagent is very costly	•recovery of sulphur as elemental sulphur is around 95%. •antimony chloride purity is relatively high (99.9%) •able to process ore with relatively high levels of arsenic.
Calcium Chlorine Roast	•bench scale development 1980.	•limited recovery of antimony to 90%. •corrosive environment at elevated temperatures (500°C).	•recycle of chlorine by calcium chloride regeneration is possible. •impurities of Pb and As are removed by distillation. •roast has been reported as autothermal.

Development strategies up to 1980 have been directed toward combining unit operations to overcome limitations of pyro-processing. Current technology is trending toward processes designed to eliminate impurities without the need for multi-stage unit operations. It is expected that future development in the processing of antimony sulphides will revolve primarily around chlorination technology due to the following reasons:

(a) Antimony complexes are not formed in a chlorine environment. The formation of antimony chloride is predominant in the chlorination of antimony sulphide.

(b) Impurities such as arsenic, iron and lead form chlorides that have unique boiling points. Therefore, impurities can be easily separated from antimony chloride in pyro-systems by distillation.

(c) Antimony metal and/or oxide can be produced at market specifications by further processing of antimony chloride. The metal is formed by reduction of the trichloride by electrolysis and the oxide is produced by hydrolysis.

(d) Sulphur can be recovered in its elemental form.

(e) Lower capital investments are required for chlorination-electrowin- hydrolysis when compared to high temperature oxidation operations.

3.0 HYDROMETALLURGICAL PROCESSING

Recent development of hydrometallurgical (hydromet) processing technology has focused on the production of antimony metal by electrowinning, and the extraction of mercury and silver from complex antimony ores. Changing demand for high purity antimony metal and trioxide, together with government imposed regulations on sulphur emission, has increased the incentive for further development in this field. For hydromet processing to successfully compete against conventional pyrometallurgical production, the following criteria must be met:

(a) Sulphur must be recoverable in elemental form or as a marketable compound.

(b) Purity and recovery of antimony products must match or exceed those achieved by pyrometallurgical methods.

(c) Capital and operating costs must be competitive and the process must be capable of producing both metal and trioxide.

(d) Environmental control of impurities must be integral with the process.

(e) Market confidence must be established. End users must be assured of the continuity of quality products with the changing technology.

3.1 Sodium Sulphide Systems

The Quelar process uses a sodium sulphide leach with the addition of sodium hydroxide prior to solution electrolysis. Antimony metal is electrowon at the cathode and sodium sulphide is recovered as a by product. Figure 11 is a typical Quelar Process flowsheet.

The Quelar process patent was developed on antimony sulphide concentrate assaying 61% Sb and 4.5% arsenic. Typical operating parameters include primary leaching at 75°-80°C and 250 g/L Na_2S to produce a solution containing 250-300 g/L antimony. Electrolysis is at 50°-60°C at a current density of 10 amps/square foot. Cooling of the electrolyte results in sodium sulphide crystallization. Na_2S crystal produced by this method typically assays 0.05% Sb.

Process economics are dependent to a large degree on the co-production of sodium sulphide. For each tonne of antimony metal produced, 1.5 tonnes of sodium sulphide are recovered. Reagent costs are extremely high (0.63 tonnes of NaOH consumed per tonne of metal produced) with power consumption reportedly in the 0.35 KWH/kilogram range.

The capital outlay for a primary leach circuit of 500 cubic metres for a 30 tonne per day operation would be significant. Leaching times (primary) up to 48 hours in duration at 80°C dictate the need for substantial capital investment for large heating units.

A version of the Quelar process described is used by Sunshine Mining Company, Big Creek, Idaho, to produce antimony metal assaying about 96% Sb and 3.5% arsenic. Further processing is required to produce oxide from the metal.

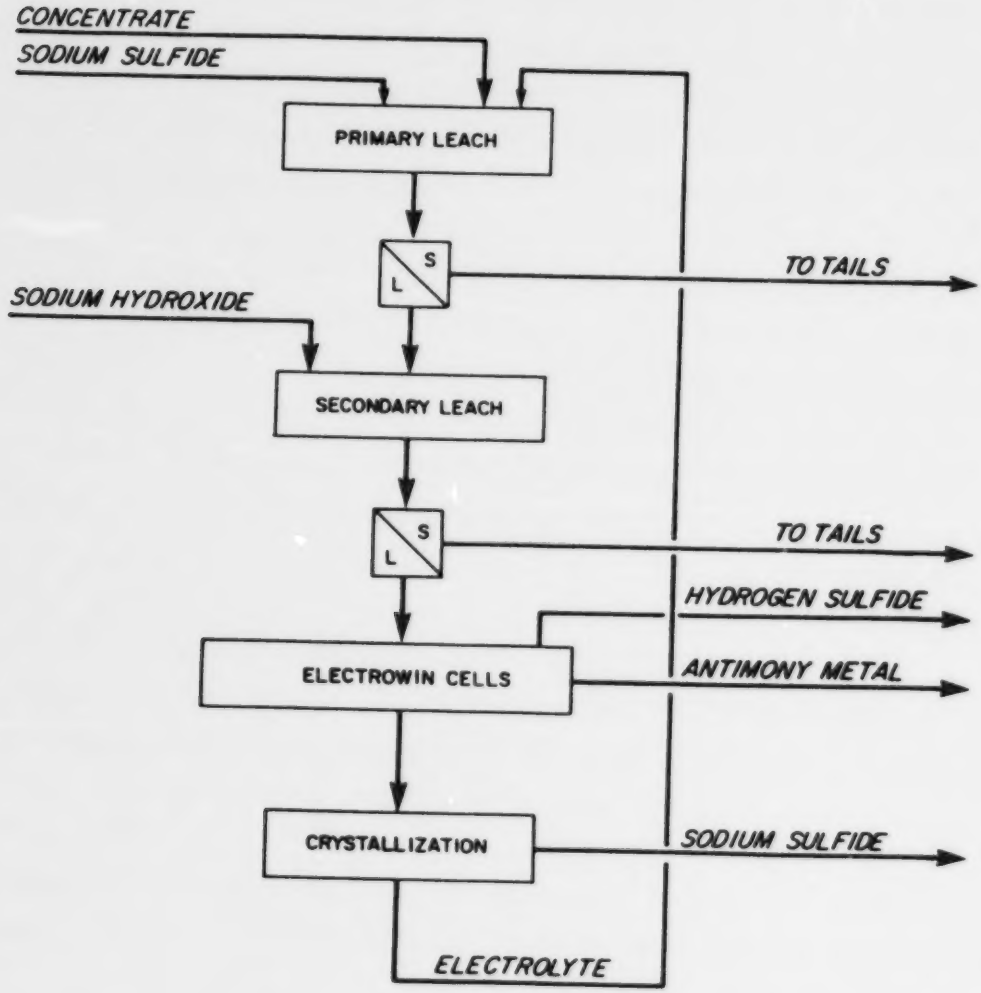


Figure 11. Process Flowsheet of the Quelar Process Using a Sodium Sulfide-Sodium Hydroxide Leach Circuit with Electrowinning of Solution to Produce Metal. (Ref. 35)

3.2 Chloride Systems

Chloride leach-electrowin technology has been known since the 19th century. However, the development of a commercialized process has been limited due to the corrosive nature of chlorine. Conventional materials of construction used for agitators and tanks, such as stainless steel, Hastalloy C and rubber-lined carbon steel tanks, all have limited life in a chloride environment. Recent developments in titanium alloys and high temperature plastics have increased the prospects for commercial chloride processing systems.

The chloride process developed by Rud. Koepp and Co. in 1892[11] included the leaching of antimony sulphide using ferric chloride as a leachant at 85°C. The following reaction describes the chemical process:

$$6FeCl_3 + Sb_2S_3 = 6FeCl_2 + 2\ SbCl_3 + S_3$$

The resulting antimony chloride solution was subjected to electrowinning using lead plates at 3.7 amps/sq. ft. to produce antimony metal and chlorine gas. Grade and recovery of antimony were not reported.

Bench scale research[6] of ferric chloride leach rates on stibnite show that reaction rates are predominantly controlled by diffusion of the reductant (Fe^{III}) throughout the sulphur layer. These results suggest that leaching rates are strongly dependent on leachant concentration, leach temperature and particle size. Previous work has indicated that optimum conditions include a $FeCl_3 : Sb_2S_3$ molar ratio of 9 at 103°C when combined with 1.3 moles of HCl and 2.5 moles of NaCl. Additional research on methods to produce antimony oxide and/or metal from these leach solutions has not been reported.

Recent developments in the production of antimony trioxide from the hydrolysis of antimony chloride in aqueous ammonia solutions makes chloride technology commercially attractive. The hydrolysis of antimony chloride results in light sensitive oxide which darkens on exposure to light. However, Occidental Petroleum[15-17] have developed a procedure for the production of senarmontite which is light stable. The process, shown in Figure 12, takes place according to the following reaction:

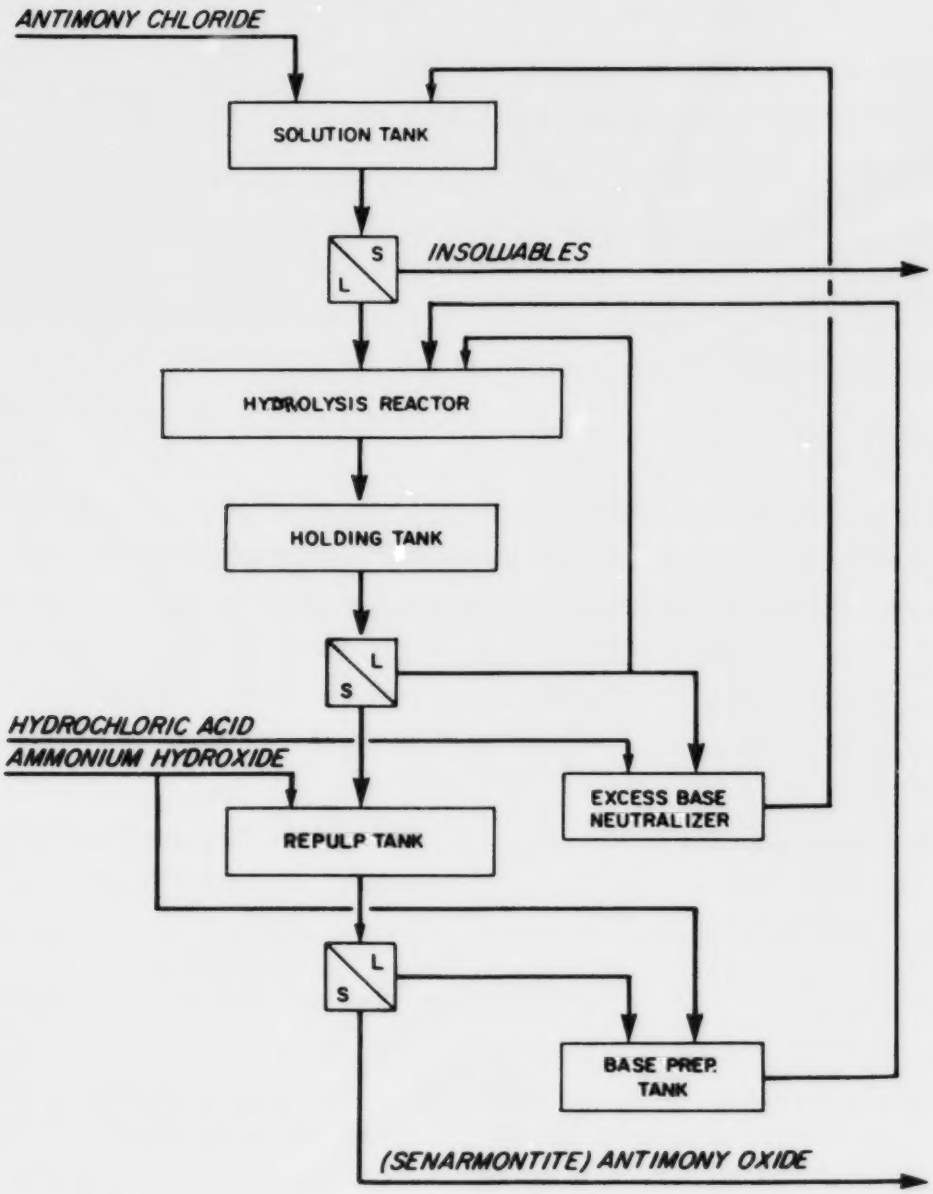


Figure 12. Process Flowsheet for Hydrolysis of Antimony Chloride, Occidental Petroleum Patent (Ref. 15).

$$2SbCl_3 + 6NH_3 + 3H_2O = 5NH_4Cl + 2Sb_2O_3$$

Antimony chloride, dissolved in water in a ratio of 9:1 ($SbCl_3$:H_2O), is filtered to remove fine solids and then passed through a hydrolysis reactor to produce antimony trioxide under the following conditions:

(a) temperature less than 40°C.

(b) aqueous basic solution pH 8-9 (NH_4OH).

(c) aqueous chloride solution of NH_4Cl (3-5 molar).

(d) reaction time 10-30 minutes.

Particle size of the hydrolysis product is in the range of 1-10 microns. The resulting ammonium chloride solution is filtered and used to control chloride concentration in the solution tank. The presence of excess water results in the formation of antimony oxychlorides. An excess of free chloride ion prevents hydrolysis product formation. A second filtration stage is required to wash the oxide cake at pH 11. Purity of the oxide in excess of 95% senarmontite has been reported with a 99% antimony recovery.

A major advantage of chloride hydrometallurgy is that antimony metal, antimony trioxide, and elemental sulphur are produced. Future development in chloride hydrometallurgy should focus on:

(a) Regeneration of chloride leachant - the economics of ferric chloride hydrometallurgy depends on the ability to regenerate leachant.

(b) Complex ores - the ability for chloride leach systems to treat complex ores (where stibnite is bound to various other sulphide or sulfantimonide minerals) requires further testing.

(c) Purification of antimony chloride - for efficient hydrolysis of antimony chloride solutions, purification methods to remove arsenic, lead, copper, zinc, and iron are required. It should be noted that the hydrolysis process, with high ammonium chloride concentrations, results in high solubilities of arsenic (22.5 g/L). Antimony trioxide has a solubility of 0.0083 g/L. Iron is the most troublesome contaminant in hydrolysis unit operations.

(d) Leach residue treatment - if economic levels of precious metals are present in the residue prior to the extraction of silver and gold by cyanide leach.

3.3 Ammonium Sulphide Systems

Ammonium sulphide leach-oxidation to produce antimony trioxide has been developed[1] and pilot tested. The process involves leaching stibnite concentrate with ammonium sulphide and ammonium hydroxide at 90°C for 3 hours. Sulphur is added to the leach solution to increase the solubility of antimony sulphide. The leach solution is then separated from insoluble gangue by distillation. A nitric acid solution (up to 20% HNO_3) is used as an oxidant to produce antimony trioxide.

Processing limitations of this system are low sulphur recovery and the uncontrolled formation of various oxides of antimony. Sulphur removal by solvent extraction is a costly unit operation as is the scrubbing associated with H_2S and nitrous oxide gas recovery and control.

3.4 Other Leaching Methods

Experimentation to recover antimony from sulphide ores using other leachants includes:

(a) Hydrochloric acid - hot hydrochloric acid will extract antimony from powdered ore and, when neutralized with lime, produce an antimony precipitate. Addition of large amounts of water to chloride solutions precipitates antimony as an oxychloride.

(b) Sodium hydroxide - has been found to selectively extract antimony oxide from ore. Hot caustic leach, (2% NaOH at 100°C) followed by carbon dioxide addition, precipitated antimony sulphide.

(c) Sulphuric acid - a hot concentrated acid solution is required to form a solution of antimony sulphate.

3.5 Summary of Hydrometallurgical Methods

Technology for producing high grade antimony trioxide as well as high purity metal by chemical methods is being developed. Feedstock grade is not as sensitive to reaction kinetics in hydrometallurgy as with pyro processing. However, additional hydromet unit operations are required to remove impurities from leach solutions. To date, limited technology has been developed on impurity removal from antimony leach solutions. Data on product purities and yield have not been published on secondary reactions which occur in hydrometallurgical operations. Hydromet technologies developed to date are summarized in Table 7. Current major limitations to these methods are leachant regeneration and impurities removal from leach solutions. Chloride hydrometallurgy indicates definite processing advantages but process development is required.

4.0 ANTIMONY PRODUCTS PLANT

The feasibility of a Durham Resources antimony products plant (DRAPP) located at the Lake George Mine is dependent upon the current technology selection for oxide and/or metal production as well as product marketability. Three options have been selected for a preliminary study of techno-economic feasibilities.

The production of metal from high grade concentrates with limited sulphur dioxide emissions was bench tested by DNRE and scaled up for commercial production using the English Precipitation method. The economics of producing crude oxide using rotary kiln methods were reviewed by DNRE. Ferric chloride hydromet technologies were developed by bench testing at the DNRE laboratory. Some technical-economic limitations of each method were discussed earlier in this paper.

As stated above, limiting factors of an antimony products plant are the selling price (or add-on value) of the product and the established marketing structure for these products. The relationship between the selling price of concentrate, oxide and metal is not a constant.

Table 7. Summary of Hydrometallurgical Processing of Antimony Sulphide

Process Technology	State of Development	Process Limitations	Process Advantages
Sodium Sulphide (Quelar Process)	•1970 patent, commercialized by Sunshine Mining Co.	•cells will generate H_2S. •economics based on marketing Na_2S by-products. •high leach times, utilizes high heat demand and increases equipment capital. •additional unit operations to produce oxide from metal (pyro-technology required).	•metals produced at high purity and yield in excess of pyro methods. •low power requirements.
Ferric Chloride	•1892 patent, bench development (not optimized) Rud. Koepp Co.	•corrosive environment. •process not developed with respect to antimony extraction and removal of impurities.	•elemental sulphur as by-product. •antimony chloride produced which oxide or metal can be further produced.
Hydrolysis of Antimony	•1973 patent, bench development by Occidental Petroleum.	•production of antimony chloride not fully developed •requires close control of hydrolysis conditions.	•marketable oxide produced. •will reduce arsenic impurities by solubility difference.
Ammonium Sulphide	•1970 patent, bench and pilot plant developed.	•removal of sulphur by solvent extraction not economical. •high H_2S levels from leach-oxidation. •various oxides result in product using nitric acid. •large requirements for off-gas scrubbing (H_2S and NO_x).	•purification of stibnite from gangue.

In considering the selling price of concentrate versus the add-on value of oxide and/or metal, the maximum production cost of an antimony products plant can be evaluated.

Maximum production costs for metal, as shown in Figure 13, indicate that metal prices would have to be in the range $US 1.70/lb to $US 1.82/lb to make metal production viable with concentrate selling for $US 18.00 to $US 19.50 per MTU. On the other hand, the ideal maximum production cost for oxide, shown in Figure 14, is around $US 0.15/lb oxide ($CDN 0.20/lb oxide) for the same concentrate selling price.

Market availability is considered to be a major drawback to a Durham Resources owned antimony products plant. Total known world smelter capacity for all antimony products was 93,713 tonnes in 1984. Durham Resources has a production potential of 4,360 tonnes of antimony which equates to about 5% of world smelter capacity. Market demand is forecast to increase some 6000 tonnes by 1990.

The marketing opportunities and flowsheet design for a multi-product facility is beyond the scope of this study. However, the technology for a conceptual flowsheet will be addressed. It is recognized that market opportunities will have to be established before an actual flowsheet can be devised.

Feedstock variation has not been addressed by this study with respect to economics, availability and type. An antimony products plant at Durham resources must be met by the assurance of a (continued) supply of feedstock to ensure long term profitability. Only high grade flotation concentrates from the Durham concentrator, as illustrated in Table 8, were considered for this study.

4.1 English Precipitation Melt

The English precipitation melt (EPM) was bench tested at DNRE to quantify the grade-recovery limitations of metal production from high grade antimony sulphide

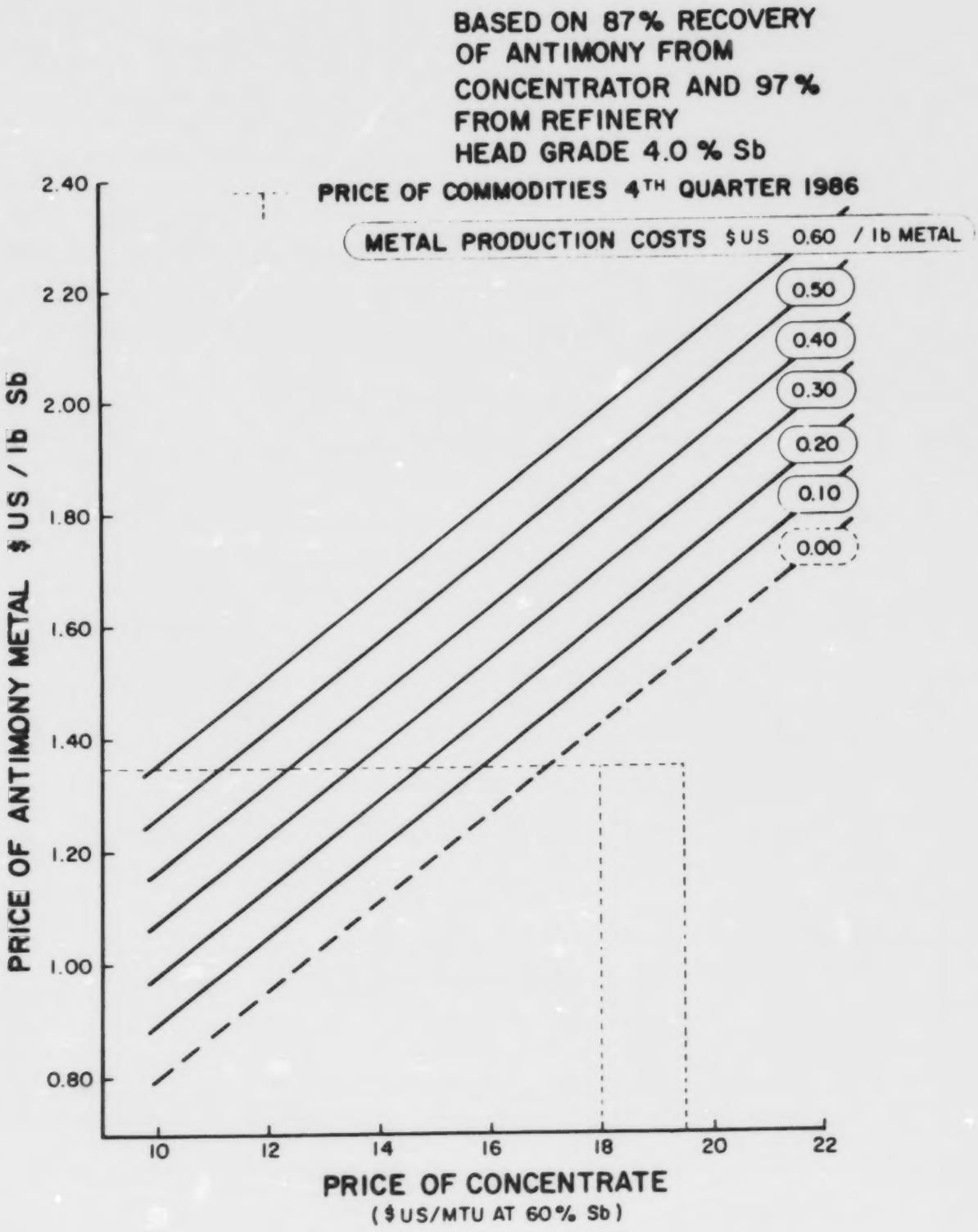


Figure 13. Maximum Production Cost of Antimony Metal Versus Market Values of Metal and Antimony Sulfide Concentrates.

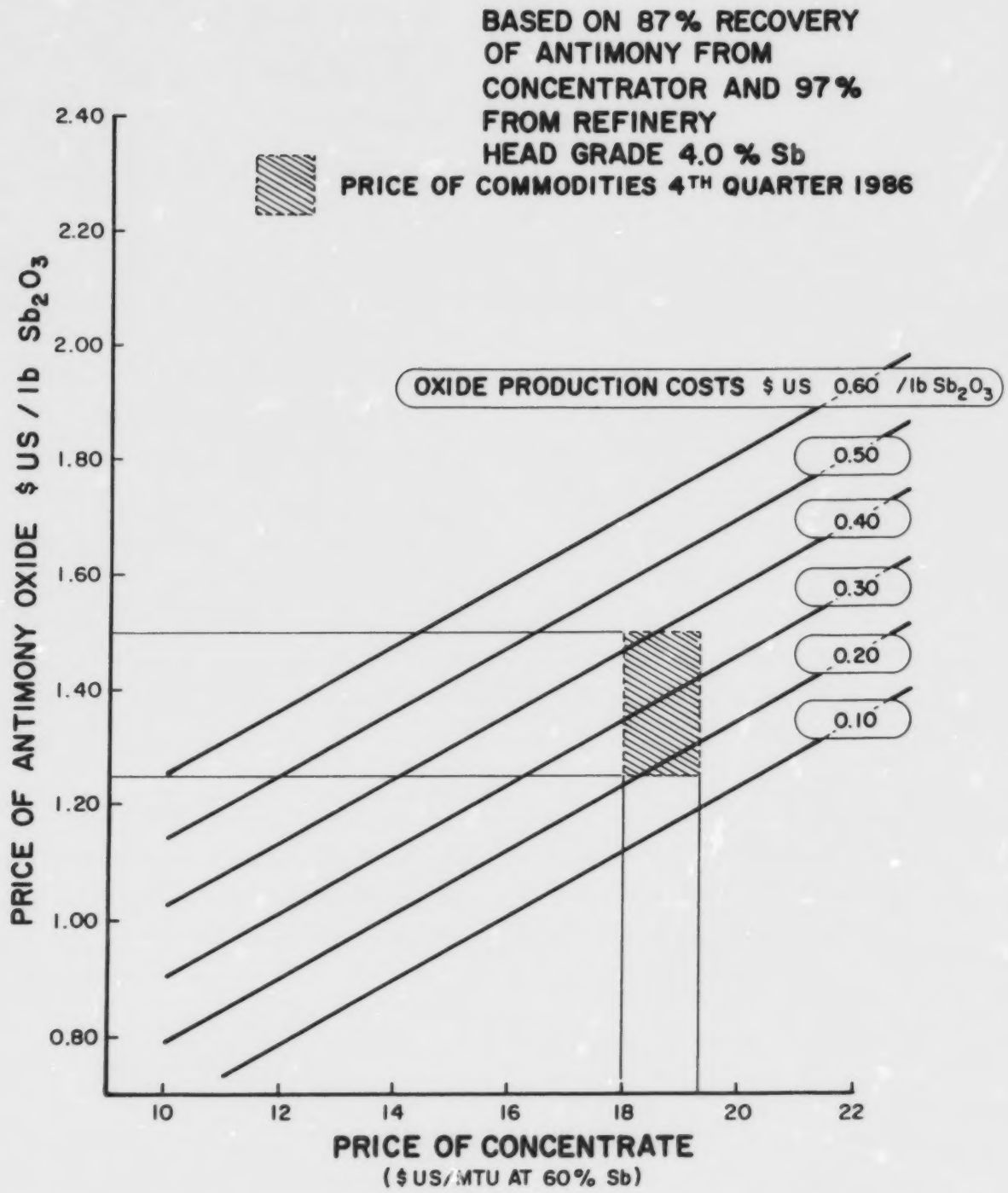


Figure 14. Maximum Production Cost of Antimony Trioxide Versus Market Values of Oxide and Antimony Sulfide Concentrates.

Table 8. Mineralogy and Particle Size Distribution of Antimony Flotation Concentrates (Lake George Mine)

(Weight Distribution, measured in area %)		
Mineral Type (majority)	High Grade Concentrate (66% Sb)	Low Grade Concentrate (55% Sb)
Stibnite	84.67	77.80
Native Antimony	0.26	7.85
Iron rich stibnite (5% or more Fe)	1.60	2.51
Berthierite/Gudmundite	0.21	1.19
Quartz	10.37	7.32
Calcite	0.20	0.34
Pyrite	1.12	1.66
Arsenopyrite	0.03	0.01
Feldspar	0.01	0.02
Muscourite/Chlorite	1.46	1.29
Sphalerite	0.07	0.01
Total	100.00	100.00

Assay and Weight Distribution of Metal in Rougher (RO) and Cleaner (CL) Concentrates

Particle Size (microns)	Assay % Sb (antimony)		Metal Distribution (% wt)	
	RO	CL	RO	CL
+149	36.5	51.2	0.40	1.22
100-149	55.8	60.2	3.08	4.72
75-100	58.1	65.3	6.99	9.01
44-75	60.3	67.8	16.21	21.53
37-44	61.2	68.1	6.94	2.77
25-37	56.3	67.5	10.16	10.85
-25	41.3	63.6	56.21	49.91

concentrates from the Durham concentrator. The fundamental theory of the melt is outlined in Section 2.2.1.

Normal test conditions were selected based on commercial operations as reported in the literature. A cast iron pot (2.5" x 4") was used to melt 250 g of concentrate, assaying 62.3% Sb and 0.27% As, in a muffle furnace. The melt was stirred every 15 minutes to assure a homogeneous mixture within the slag. Metal was poured from the pot for each test using a ladle to hold back slag. The metal buttons were cooled and then drilled to produce metal shavings for assay. Slag was ground to 110 mesh to enable representative sampling to take place. Results of each test are summarized in Table 9.

4.1.1 Series A. Normal Conditions, Duplication of Tests

Under normal (from the literature) operating conditions the recovery of antimony is limited. Arsenic content in the metal is too high which makes the product unsaleable. See Table 3 for product specifications. Tests in this series were easily reproduced. Average grades obtained were 96.5% ± 0.90% antimony and 0.54% ± 0.05% arsenic with average recoveries of 57.3% ± 3.8% antimony and 73.4% ± 9.5% arsenic.

4.1.2 Series B. Variation of Conditions for Melt

Conditions were varied from the normal recipe for Test 5 through Test 16. Varying the concentration of fluxing agents in Tests 5 through 8 resulted in no separation of metal from slag. Antimony metal was dispersed throughout the slag in small balls (0.5-1 mm). It is believed that the slag became very viscous thereby not allowing the metal to sink.

The use of Woodstock Manganese ore as a source of iron in Tests 9 and 10 resulted in improved recovery at a temperature of 1000°C. (The use of manganese ore is a possible source of iron if the English precipitation melt proves feasible for commercial production.)

Table 9. English Precipitation Melts on Durham Antimony Flotation Concentrate (62.3% Sb, 0.27% As) Normal Conditions at 800°C, 1.5 hr Healing, 250 g Concentrate)

Test Conditions	Carbon g	Sodium g	Iron g	Slag Weight g	Slag Assay %Sb/%As	Metal Weight g	Metal Assay %Sb/%As	Recovery %Sb/%As
SERIES A - NORMAL CONDITIONS								
1. Norm Recipe	17.0	62.5	82.5	263.0	26.7/0.06	95.3	96.1/0.56	58.8/79.1
2. Norm Recipe	17.0	62.5	82.5	272.4	20.7/0.08	101.8	96.3/0.55	62.9/82.9
3. Norm Recipe	17.0	62.5	82.5	298.1	28.4/0.08	87.4	96.2/0.49	54.1/63.4
4. Norm Recipe	17.0	62.5	82.5	290.4	26.2/0.10	85.5	97.4/0.54	53.5/68.4
SERIES B - VARIATION OF CONDITIONS								
5. Lower Na	17.0	37.5	82.5	No Sep.				
6. NO Iron	17.0	62.5	0.0	No Sep.				
7. Double Iron	17.0	62.5	105.0	No Sep.				
8. Lower Iron	17.0	62.5	41.3	216.0	29.5/0.05	89.7	93.8/0.44	54.0/58.5
9. Mn Ore (160 g)	17.0	62.5	0.0	No Sep.				
10. Mn Ore (1000°C)	17.0	62.5	0.0	298.0	19.4/0.07	133.5	96.0/0.30	79.0/ -
11. Preheat 300°C	17.0	62.5	82.5	319.1	23.5/0.21	53.1	97.6/0.52	33.2/40.9
12. $CaCO_3$ (86 g)	17.0	0.0	82.5	No Sep.				
13. Lower Na,Fe	17.0	31.0	41.3	No Sep.				
14. Inter Na,Fe	17.0	45.0	41.3	285.1	38.2/0.06	74.0	96.6/0.57	46.4/62.5
15. 1000°C	17.0	45.0	41.3	193.0	-	140.0	97.8/0.30	87.9/62.2
16. No Carbon	0.0	45.0	41.3	249.0	40.4/0.07	36.0	97.6/0.65	22.6/34.7
SERIES C - REMELT OF SLAG (RECOVERY)								
17. Reagents	4.25	15.6	20.6	No Sep. 121 slag (Blend 1-4)				
18. Reagents	8.50	31.2	41.2	No Sep. 81 g slag (Blend 1-4)				
19. Red. Na/Fe	4.20	22.5	26.6	No Sep. 47 g slag (Blend 1-4)				
20. Same as 17 at 1000° C	4.25	15.6	20.6	No Sep.				
SERIES D - REFINE METAL (GRADE)								
21. 30 g metal/60 g slag (from Test 4)				64.20	34.1/0.06	25.5	98.8/0.52	86.2/81.9
22. Using 3 g potash; 60 g metal & 10 g slag				20.00	24.9/0.04	71.5	97.3/0.48	93.3/79.3
23. Using 6 g sodium carbonate, 3 g nitrate, 60 g metal and 10 g slag							98.0/0.35	
24. No slag 60 g metal	2.0	6.0	6.0	0.0	-	63.9	93.3/0.48	

A preheat was done in test 11 at 300°C for 2 hours in an attempt to volatilize the arsenic prior to the melt. This was not successful.

Increasing the temperature to 1000°C (Test 15) increased the antimony recovery to 87.9%. The elevated temperature possibly improved slag viscosity enabling effective separation of metal from slag by gravity. Recovery seems also to be controlled by the reducing agent (carbon). Test 16 gave an antimony recovery of only 22.6% with no carbon in the melt.

4.1.3 Series C. Remelt of Slag

Attempts to remelt the slag and recover the metal in Tests 17 to 20 were unsuccessful. The slag was ground to -100 mesh and remelted using fluxing agents. It appeared to be quite stable and recycling to improve metal recovery does not appear to be technically viable.

The slags produced from various melts were bench tested in a simulated tailing disposal site with no modification to pH. Over a period of 120 days, with agitation every five days, assays of the solutions shown in Table 10 indicated no potential environmental problems with water discharge.

4.1.4 Series D Refining of Metal

Metal upgrading, or refining, was attempted in Tests 21 to 24. A marginal improvement was noted in Test 21 and 23 but product values remained below market requirements.

It can only be concluded that concentrates must be arsenic free to produce market grade metal using the English precipitation melt.

Table 10. Simulated Slag Tailing Disposal. Water Sample Analysis

(120 Day Pond Simulation)				
	ASSAY mg/L			
METAL	MANGANESE SMELT (TEST 10)	NORM SMELT (TEST 2)	LOW IRON SMELT (TEST 8)	HIGH TEMP SMELT (TEST 15)
Cu	0.034	0.066	0.097	N.D.
Fe	0.110	0.191	0.239	0.118
Ni	0.054	0.179	0.406	-
Pb	<0.100	<0.100	-	-
Zn	0.037	0.126	0.176	N.D.
Cd	<0.100	<0.100	-	-
Al	0.260	N.D.	N.D.	N.D.
Sb	N.D.	N.D.	N.D.	N.D.
As	N.D.	N.D.	N.D.	N.D.
pH	10.01	10.85	10.99	9.36

N.D. - Not Detected

4.1.5 Production Costs

The cost of commercially producing antimony metal at Durham Resources antimony mine is summarized in Appendix I. Design is for a batch operation using reagent additions similar to the English precipitation melt. An induction furnace is selected to ensure rapid melting of the charge.

About 32,157 lb of metal/per day can be produced based on an annual availability of 95% and on overall DRAPP metal recovery of 80%. Two 750 KW furnaces, each sized for 6700 lb per melt, will provide a total of 20 melts per day. The capital cost estimate is around $CDN 1,624,950 $\pm$ 35% with an operating cost of $CDN 0.3499/lb metal. Overall operating cost including capital payback (11% interest over 4 years) is $CDN 0.4102/lb metal, not including the cost of feedstock.

4.1.6 Process Limitations

Based on the literature reviewed, the bench scale lab study, and the cost analysis of the English precipitation method (EPM), some significant technical and economic limitations have been identified in the use of the EPM technology on Durham Resources concentrates. The following characteristics of EPM are summarized as limitations to competitive processing:

a) Grade of arsenic in metal product is too high. The selective separation of arsenic and antimony does not appear to be possible using the fluxing agents required for EPM. The selective removal of low concentrations of arsenic from antimony concentrates may be technically feasible using a ferric sulphate leach, but the loss of antimony and the additional operating cost will not support the economics of metal production.

b) The recovery of antimony appears to be limited by the viscosity of the slag which can be improved by increasing temperatures in excess of 1000°C. The adverse effect of increasing operating temperatures is the cost of power (energy) to heat the melt. For the induction furnace operation, about 53% of the operating cost is the power requirements for an 1100-1200°C melt.

c) A large portion of the reagent costs for the EPM is associated with iron oxide consumption. The operating cost analysis uses the cost of iron ore and is equivalent to 19% of the operating cost. The bench scale work suggests that local manganese ore can be used as a source of iron. However, more test work is required before making a positive assertion on this.

d) At the present concentrate price of $US 19.50 MTU, the price of metal would have to exceed $US 2.10/lb to make metal production viable.

4.2 Rotary Kiln Operation

The rotary kiln is recognized as a commercial means of producing trioxide by air oxidation of high grade concentrates. A cost analysis for producing crude oxide from a single pass through a rotary kiln is given in Appendix B. This cost analysis serves as a baseline for the development of competitive processing methods.

4.2.1 Process Sizing

Data for the sizing and cost analysis of a rotary kiln-sublimation unit has been scaled up from information published[1] on a South African operating plant (See Figure 5). Design criteria focused on solids throughput, air requirements for oxidation, heat balance, and sizing of pipes for the sublimation unit. An assumption on the air requirements was based on the reactions stoichiometry and the air used as a quench. (The quench air is the air required to cool the gas stream from the kiln to achieve sublimation.) Based on reaction thermodynamics, the heat generated from oxidation is about 21% of the total heat required to maintain 1200°C in the kiln. Exhaust gas is cooled by passing it through standpipes attached to a main exhaust header. The sublimation of oxide takes place on the inside surface of these pipes and is recovered as it forms by a continuous hammering or "rapping" on the outside of the standpipes.

4.2.2 Production Cost

The cost analysis summary in Appendix B states that crude oxide could be produced at $CDN 0.1569/lb of crude oxide. Major operating costs are for fuel and manpower. Sulphur dioxide scrubbing at 80% efficiency accounts for 10.9% of operating costs. From maximum production cost relationships shown in Figure 14, a rotary kiln operation becomes profitable at $US 1.35 for trioxide and $US 19.00/MTU of concentrate.

4.2.3 Process Limitations

From the literature and from preliminary design calculations, the following limitations to competitive processing have been identified:

a) Critical design parameters for kiln-sublimation unit operations are solids throughput and heat balance. The basis for design parameters has not been published for processing stibnite and very few engineering companies have any experience with antimony plant design (as outlined in Table 5).

b) Operating parameters will have to be defined in order to identify conditions required to maintain product specifications and optimum recovery. Operating methods to refine crude will have to be defined. Refined trioxide can be produced from the refuming of crude oxide, however, operating conditions have not been published. Once operating methods have been identified, cost analysis can be used to establish production costs of marketable trioxide.

4.3 Ferric Chloride Leach - Hydrolysis (FCLH)

The technical limitations to product purity and recovery experienced in high temperature oxidation processes can be avoided by using chloride processing technology. For FCLH systems to be successful, the purity of the antimony chloride solution is essential. Recent process developments have been directed toward a flowsheet that is capable of both producing antimony chloride from antimony sulphide, and of purifying the reaction products in the gaseous phase. The literature reports that antimony sulphide can be chlorinated using high temperature (400-550°C) chlorine gas (phase reactions) or in low temperature (85-105°C) solutions of ferric chloride. Low temperature systems are limited due to iron contamination in hydrolysis and electrowinning. Processing economics comparing low and high temperature chlorination are not well known.

From an operating point of view, the low temperature chlorination may be more favourable considering the following:

1) High temperature chlorination must be carried out in a fluidized bed which requires prior drying of the concentrate.

2) Gas stream recycle requires precise temperature and volume control.

In order to evaluate the technical and economic possibilities of low temperature chlorination, a bench scale test program on ferric chloride leach-hydrolysis (FCLH) was carried out by DNRE. A conceptual flowsheet was proposed as shown in Figure 15. Substoichiometric leach and solvent extraction unit operations were used to maintain the purity of antimony chloride in solution. A solution of 40% tributyl phosphate (TBP) and kerosene was used to separate iron II from antimony III. Conditions in the leach circuit were selected to reduce iron III concentrations because iron III would be extracted when using TBP. The overall concept of FCLH was tested to determine if antimony oxide could be produced from a low temperature chlorination circuit. Conventional unit operations such as chlorination of iron and steam stripping ammonia were not bench tested. The objective of the test program was to identify limitations to this concept and provide a direction for further development of stibnite chlorination.

4.3.1 Leaching of Durham Concentrate

Various leachants were tested on Durham flotation concentrate to determine the leachability of antimony. The results of batch leach tests using ferric chloride, sodium sulphide, hydrochloric acid, and sulphuric acid are all reported in Figures 16 and 17. For each test, the ratio of leachant to concentrate was based on reaction stoichiometry and all of the antimony in the concentrate was assumed to be stibnite. Each test adhered to conventional leach conditions of 2 hours, 85°C and 25% solids. Optimum extraction of 97% was achieved over a two hour period using ferric chloride. The resulting solids were easily filtered indicating no problems with solid-liquid separation. The sodium sulphide leach was very viscous making solid-liquid separation difficult. The low extraction volume using sodium sulphide was accredited to short leach times as the literature[35] reports a 48

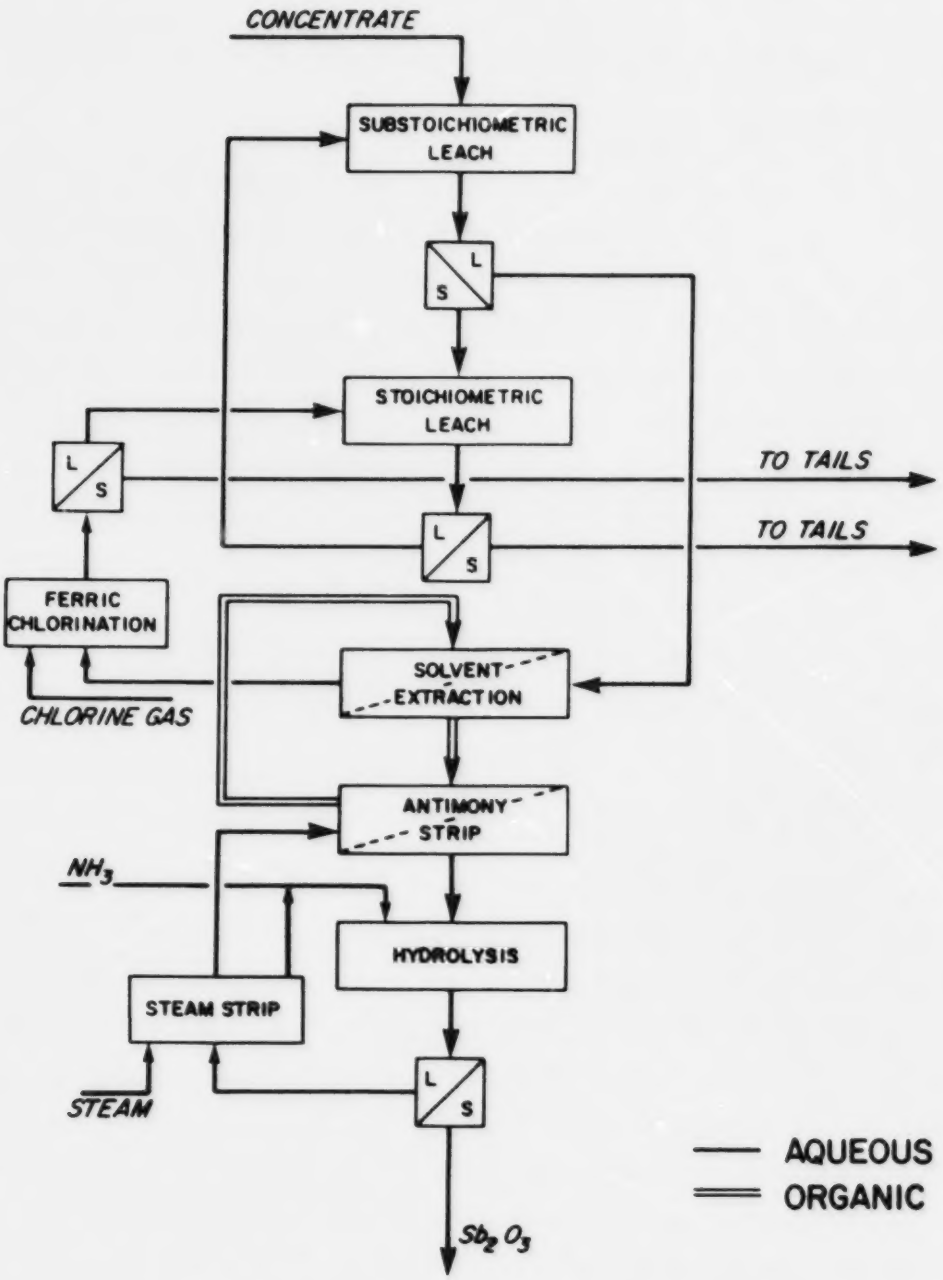


Figure 15. Process Flowsheet Concept for a Two Stage Ferric Chloride Leach, Solvent Extraction and Hydrolysis.

hour requirement to achieve 98% extraction. Limited extraction was achieved with hydrochloric and sulphuric acids.

The ferric chloride concept has been found to be an effective batch leaching method with respect to reaction time and antimony dissolution. Using a weight ratio of 5 parts of ferric chloride to one part antimony concentrate, antimony extractions ranged from 96% to 98% complete. Lowering densities from 35% to 10% solids and increasing leach temperatures to 105°C had no effect on the antimony extraction. Concentration of antimony in leach solutions reached 125 g/L. Recovery of sulphur in the residue was 75% to 80% at 85°C. Leached solids contained 62% to 66% sulphur and 3% to 6% antimony. The weight of the residue (the total chemical make-up of which was not determined) was, on the average, 30% of concentrate weights. Increasing the stoichiometry of ferric chloride to 7.9 parts ferric chloride to concentrate showed no dramatic increase in antimony extraction or sulphur recovery.

An obstacle in the ferric chloride leach-hydrolysis flowsheet is the presence of iron III in leach solutions. A two stage leach lock cycle test designed to prevent iron III from reaching the solvent extraction hydrolysis circuit was conducted using a stoichiometric leach (SL) with 4.7 Kg $FeCl_3$ per Kg concentrate and a substoichiometric leach (SSL) as illustrated in Figure 18. The overall mass balance was established from the lock cycle data of Table 11. Data from the lock cycle tests indicate that the recycle of ferric chloride (not consumed in SL) will extract 55% of the antimony in the SSL at an oxidation-reduction potential of 220 mV (moderate oxidation potential). The SSL operation converts all of the ferric ions to ferrous and exits from the leach circuit via stream 3 (Figure 18) containing approximately 52 g/L Sb. The remaining antimony in the solid residue of the SSL operation is 90% extracted at 750 mV (highly oxidizing) to give an overall extraction of 94% Sb. With further optimization of leach parameters a higher overall extraction may be achieved.

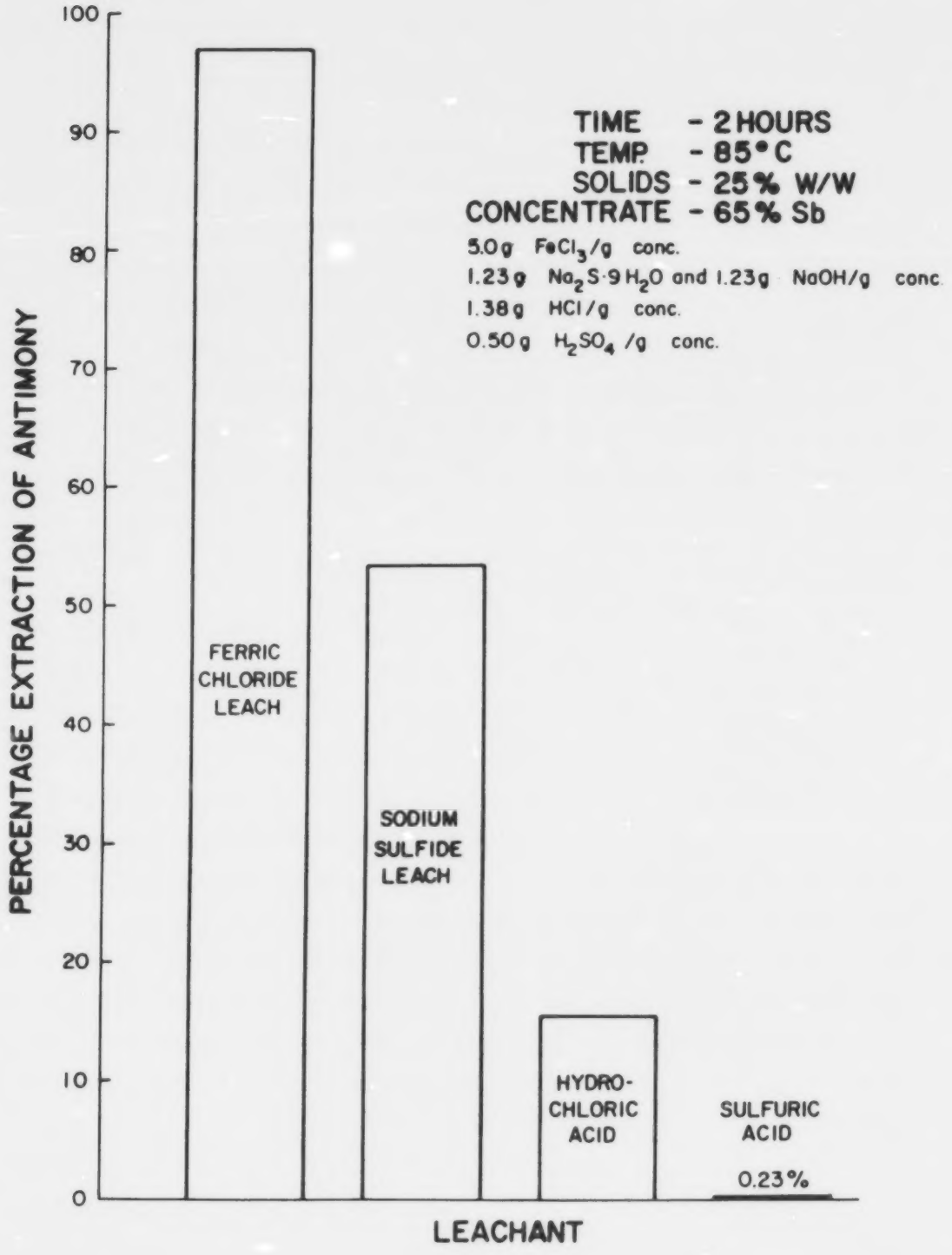


Figure 16. Extraction of Antimony Using Various Leachants at Stoichiometric Ratios.

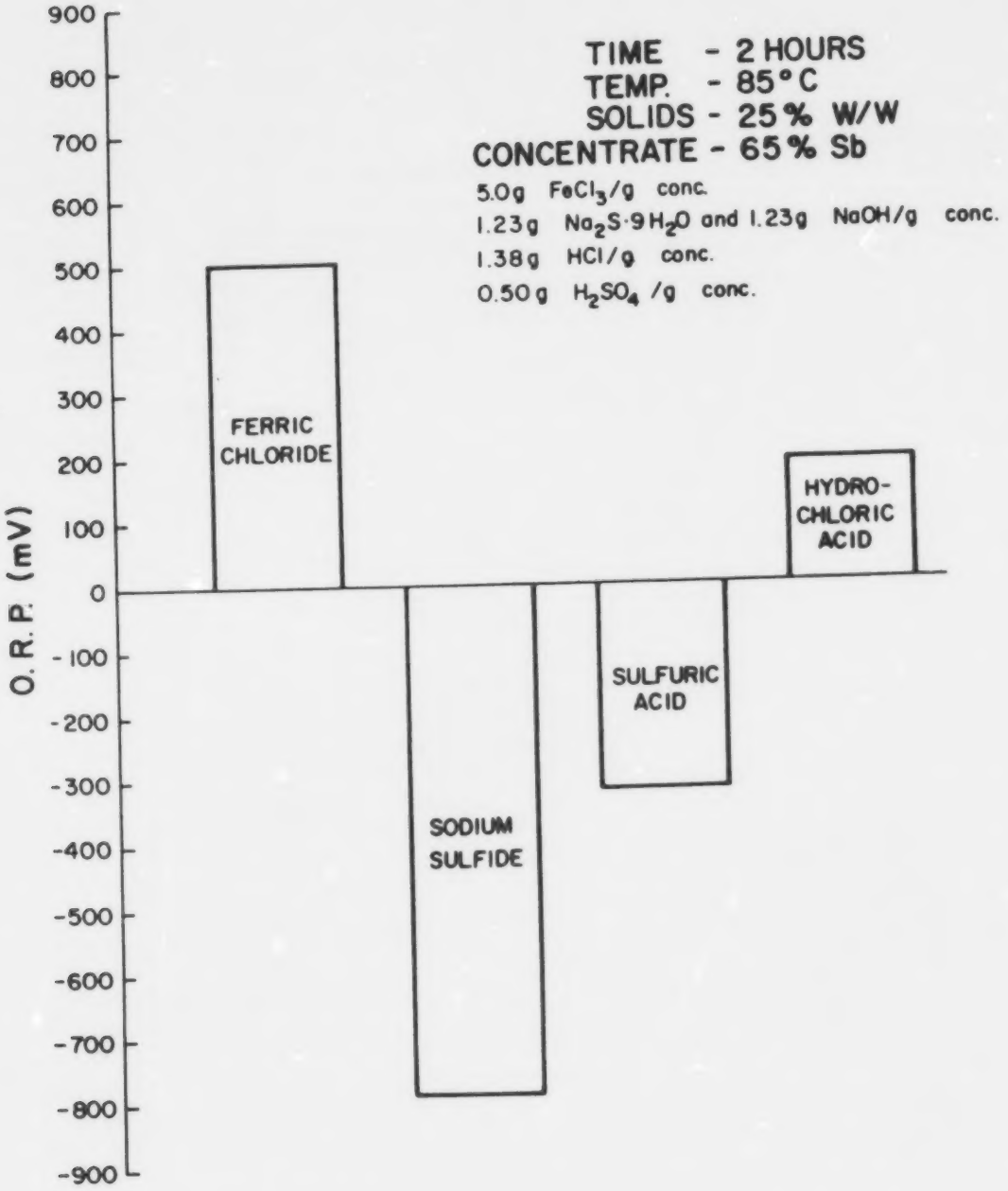


Figure 17. Oxidation/Reduction Potentials Measured in Millivolts (mv) Using Various Leachants.

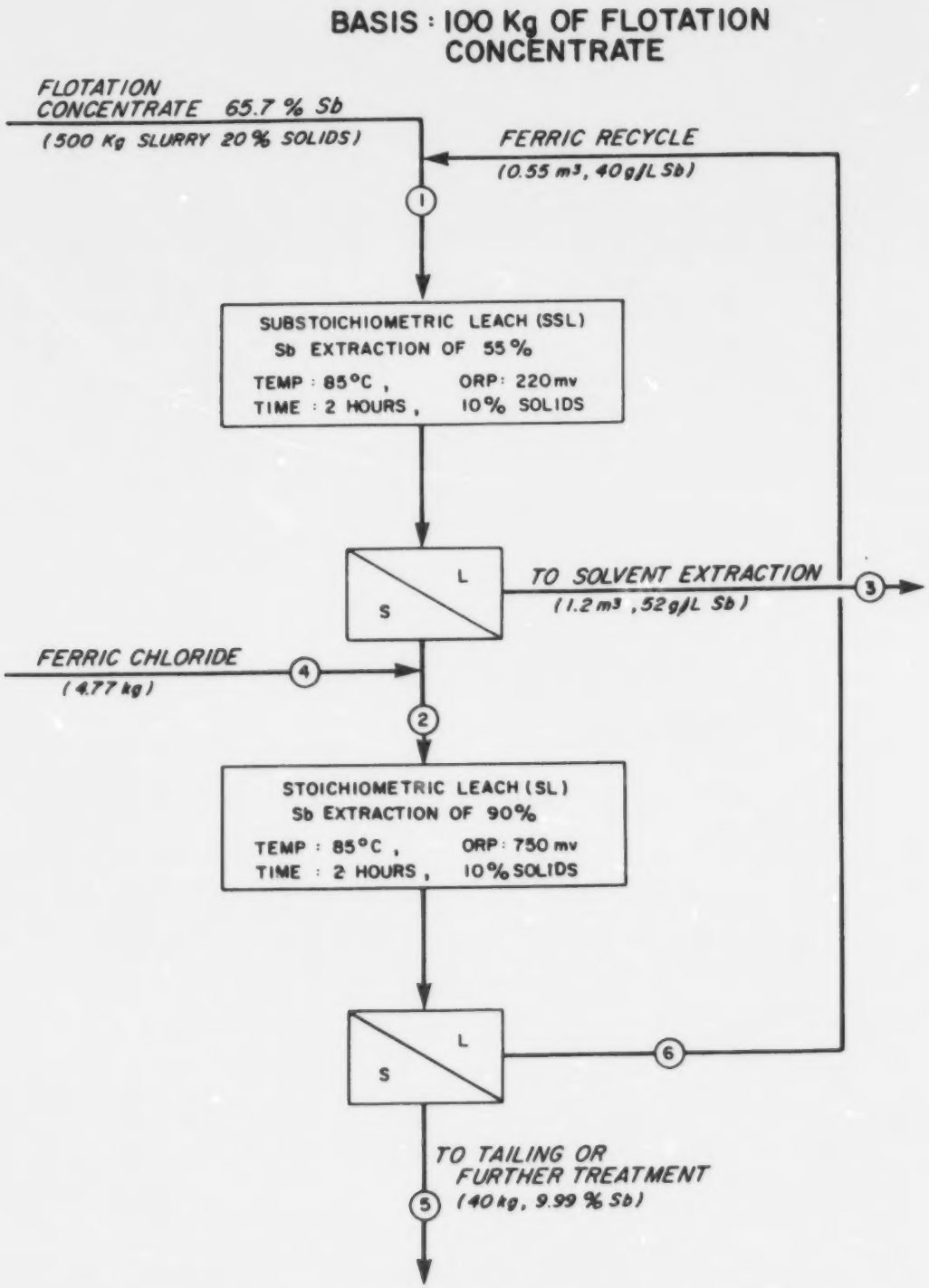


Figure 18. Flowsheet for a Two Stage Leach Circuit with an Overall Extraction of 94% (Mass Balance from Table 11).

Table 11. Lock Cycle Test on Two Stage Ferric Chloride Leach of Antimony Concentrate

STREAM NAME	CONC. FEED 1			LCH 1 SOLID 2			LCH 1 SOLN. 3			FeCl3 4			LCH 2 SOLID 5			RECYCLE 6		
	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
Weight of Soln.	400	1020	920	14.2														
Weight of Solids	100	100	100	78.1	60.6	77.4							31.5	32.7	36.8			
Percentage Solids	20	8.9	9.8	90												0.65	0.545	0.585
Volume of Soln.	400	1.02	0.92				0.32	0.93	0.698							0.65	0.545	0.585
Percentage Antimony	65.7	65.7	65.7				36.7	41.2	53.2				3.52	11.1	9.99			
Conc. Antimony		54.9	22.2				88.4	91.2	52.0							90.4	39.2	38.4
Weight of Antimony	65.7	121.75	86.1	28.66	24.97	41.17	28.29	84.82	36.3				1.11	3.03	3.67	58.74	21.36	22.46
Weight of FeCl3	262.5	787.5	420		477					787.5	420	477						
Stoichiometry*	4.0	11.9		15.15	11.5													
Oxid. Red. Potential (mv) (at 85°C)	215	223	213	765	544	755												
Sb Extraction				90.8	77.1	89.9												
Sb Balance (in = out)%	56.4 86.7	69.7 90.2	36.7 90.0	91.1	90.2	102.6												

VOLUME: L
WEIGHT: g
CONCENTRATION: g/L
EXTRACTION, BALANCE: %
*STOICHIOMETRY BASED ON WEIGHT OF FeCl3 (OXIDANT) PER WEIGHT OF Sb IN SOLID PHASE
Assay of Concentrates 65.7% Sb
Overall Extraction of 94% Based on Solid Assays (1)

4.3.2 Solvent Extraction (SX)

The solvent extraction circuit was designed to recycle ferrous ions for reuse as an oxidant in the leach. The purpose of the bench program was to investigate the technical feasibility of using 40% tributyl phosphate (TBP) in kerosene as a conventional solvent for chloride solutions and to identify technical limitations with this circuit.

TBP was chosen as a solvent because of its known selectivity between iron III and antimony III. All testing was done using a separatory funnel on batch leach solutions containing 114 g/L antimony.

A limitation to antimony recovery in the SX circuit was the formation of an antimony oxychloride precipitate. Tests involving the variation of organic/aqueous (O/A) ratios indicated a rapid absorption of antimony by the organic phase. For an O/A ratio of 2, 97% of the antimony was recovered in the organic phase as shown in Figure 19. The formation of a sludge was not acknowledged between O/A ratios from 2 to 10. At an O/A ratio of 0.50, a white precipitate formed and antimony recovery in the organic phase was low.

Low strip recoveries were experienced because of the formation of the antimony oxychloride precipitate. For O/A ratios of 2, approximately 11% of the antimony was recovered in the aqueous phase. As shown in Figure 20, an increase of O/A strip ratios results in a decrease of antimony recovery to the aqueous phase. Ammonium chloride was used in the strip solutions (230 g/L) to simulate recycle of hydrolysis solutions and to stabilize the antimony in solution by adding chloride ions.

The precipitate occurring throughout the solvent extraction circuit was isolated and analyzed by XRD. The results of the XRD scan are summarized in Appendix IVA. The complex was found to be a mixture of antimony trioxide (in the valentinite form) and antimony oxychloride having the formula $Sb_4O_5Cl_2$.

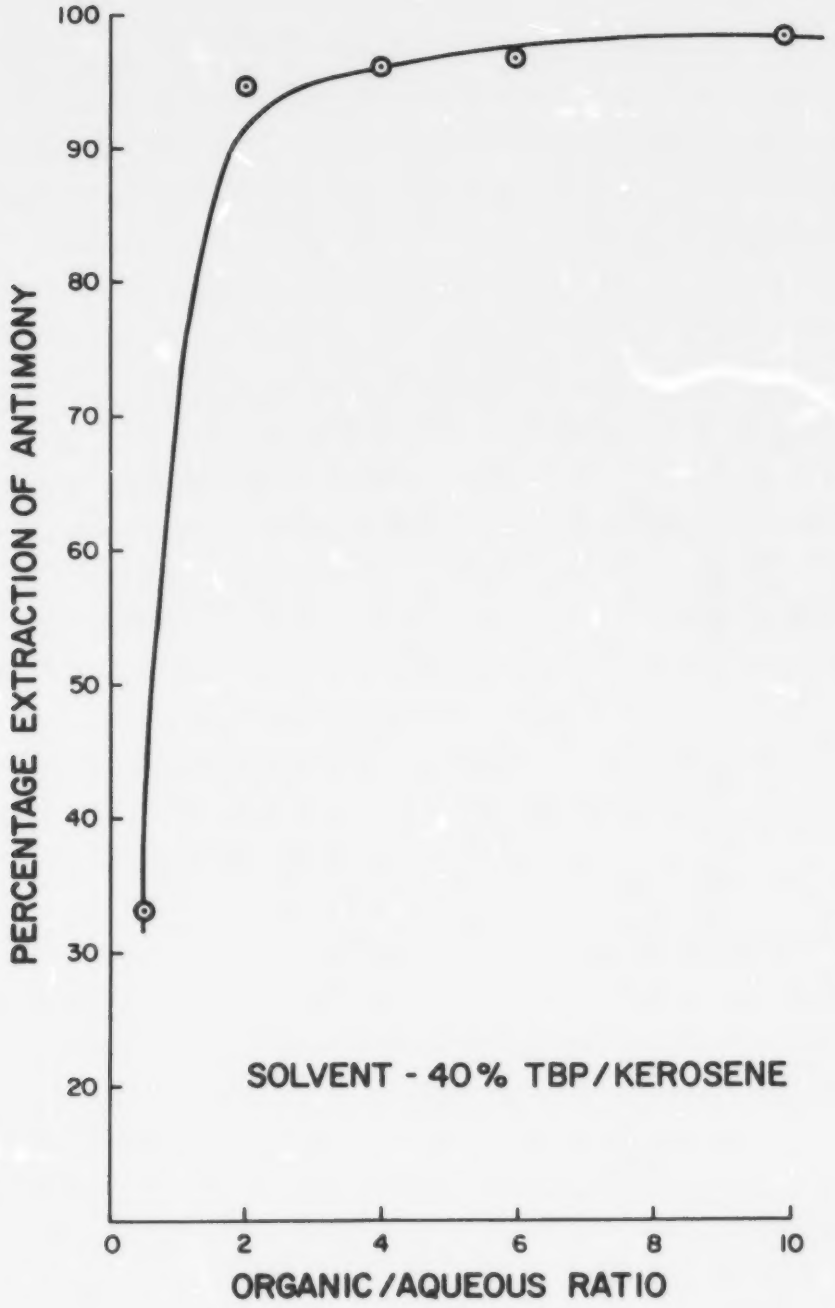


Figure 19. Extraction of Antimony (114 g/L Sb) from Leach Solution Using a Volumetric Flask at Various Organic/Aqueous Ratios.

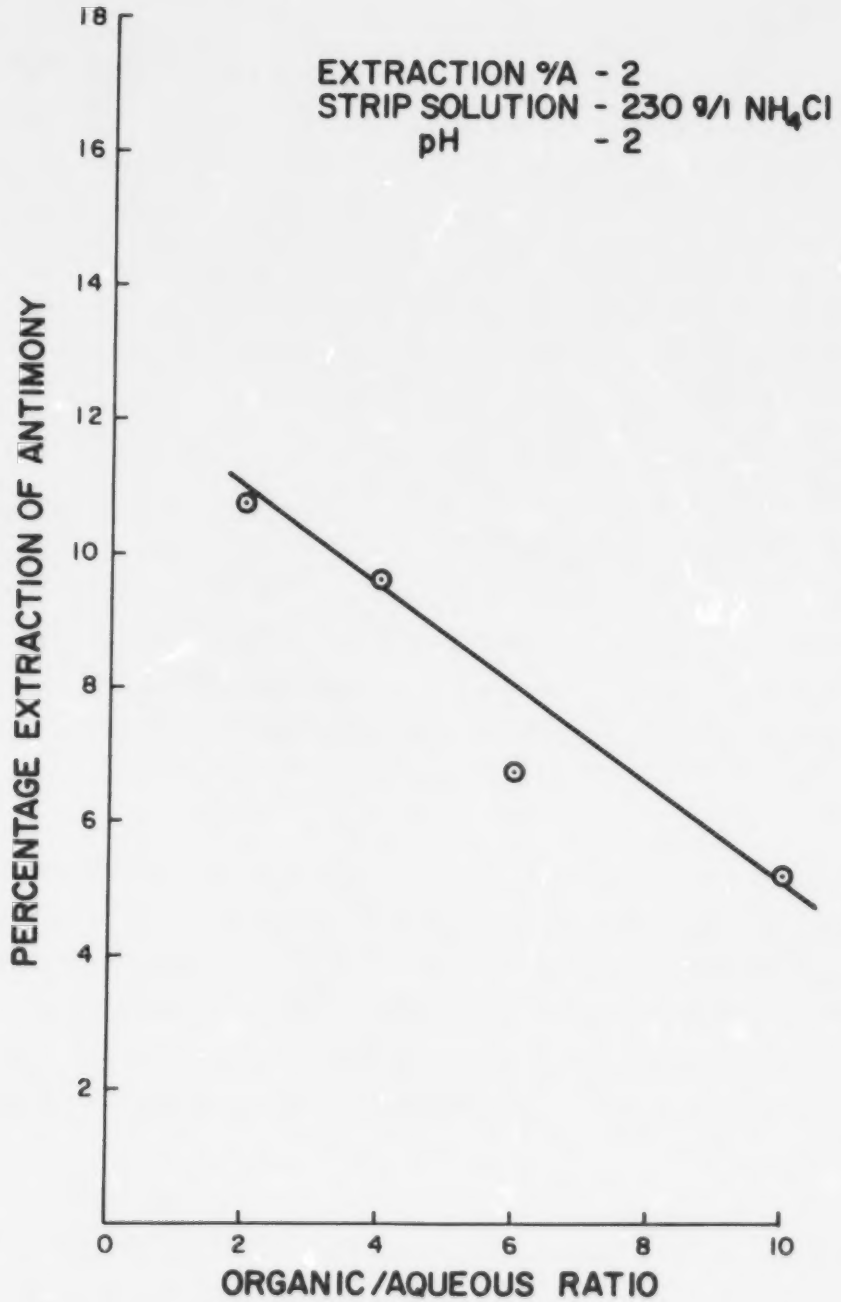


Figure 20. Stripping of Antimony (55.8 g/L Sb) from Organic Solution Using a Volumetric Flask at Various Organic/Aqueous Ratios.

The stability of antimony in solution is proportional to the chloride concentration as confirmed by adding high concentrations of chloride to the strip solution. The strip recovery was increased by doubling the NH_4CL to 450 g/L in strip solutions of an O/A ratio of 2, as shown in Figure 21. Similarly, for an O/A ratio of 6, increasing the chloride concentration also improved strip recoveries as shown in Figure 22. As outlined in Table 12, strip solutions containing 450g/L NH_4Cl at an O/A ratio of 2 did not produce a precipitate.

The effect of pH on stripping efficiency at various concentrations of ammonium chloride is shown in Figure 23. For low concentrations of NH_4Cl (less that 440 g/L) and for an O/A ratio greater than 2, the pH does not increase the stability of antimony in solution. The data does not include the effect of pH at an O/A ratio less than 2 and NH_4Cl concentrations greater than 440 g/L. It is expected that a lower pH would be favourable. However, hydrochloric acid consumption would impact negatively on hydrolysis economics.

The selectivity of both iron and antimony was tested at various organic/aqueous ratios and solution pH. The selectivity (B), plotted in Figure 24, is defined by the recovery of iron to the strip solution divided by the recovery of antimony from leach liquor to organic phase. The denominator is expressed this way because of problems with oxychloride precipitation in the strip. Results indicate that ideal conditions for SX favouring low recoveries of iron are at high O/A ratios and low pH.

An overall mass balance was determined on the solvent extraction circuit using a single stage for the extraction and strip. Optimum conditions were selected from previous test data as indicated in Figure 25. The overall extraction of 47% is limited by low stripping efficiencies. However, an understanding of hydrolysis mechanisms (specifically oxychloride formation) may be required before further work is carried out on the strip.

It was determined that the leach solution contains about 578 g/L chlorine (ratio of Sb:CL is 1:3.5). The loaded organic from the extraction picks up about 11% of the chlorine. Stripping the organic with 440 g/L NH_4Cl at an O/A ratio of 2 results in an

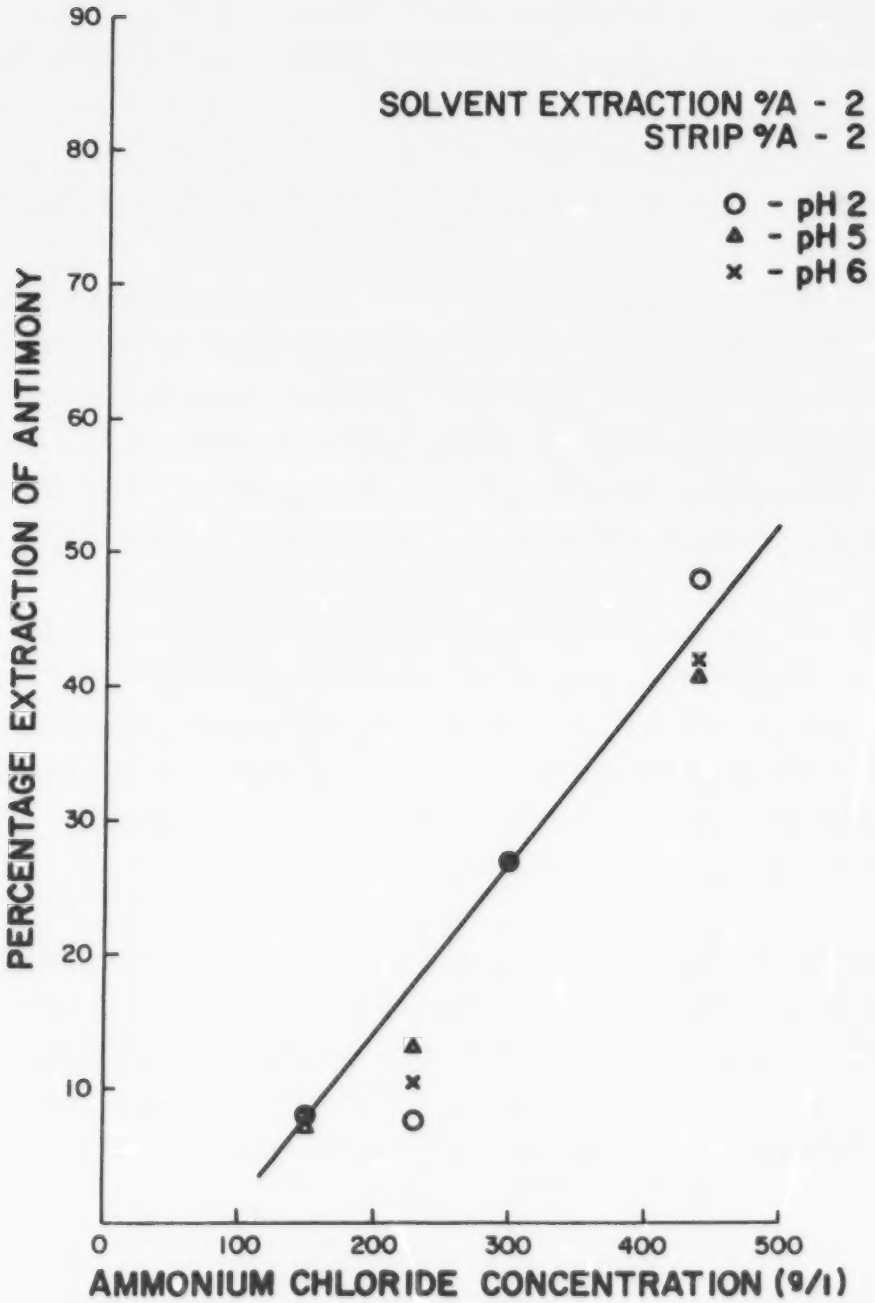


Figure 21. Stripping of Antimony (55.4 g/L Sb) from Organic Solution at Various Concentrations of Ammonium Chloride.

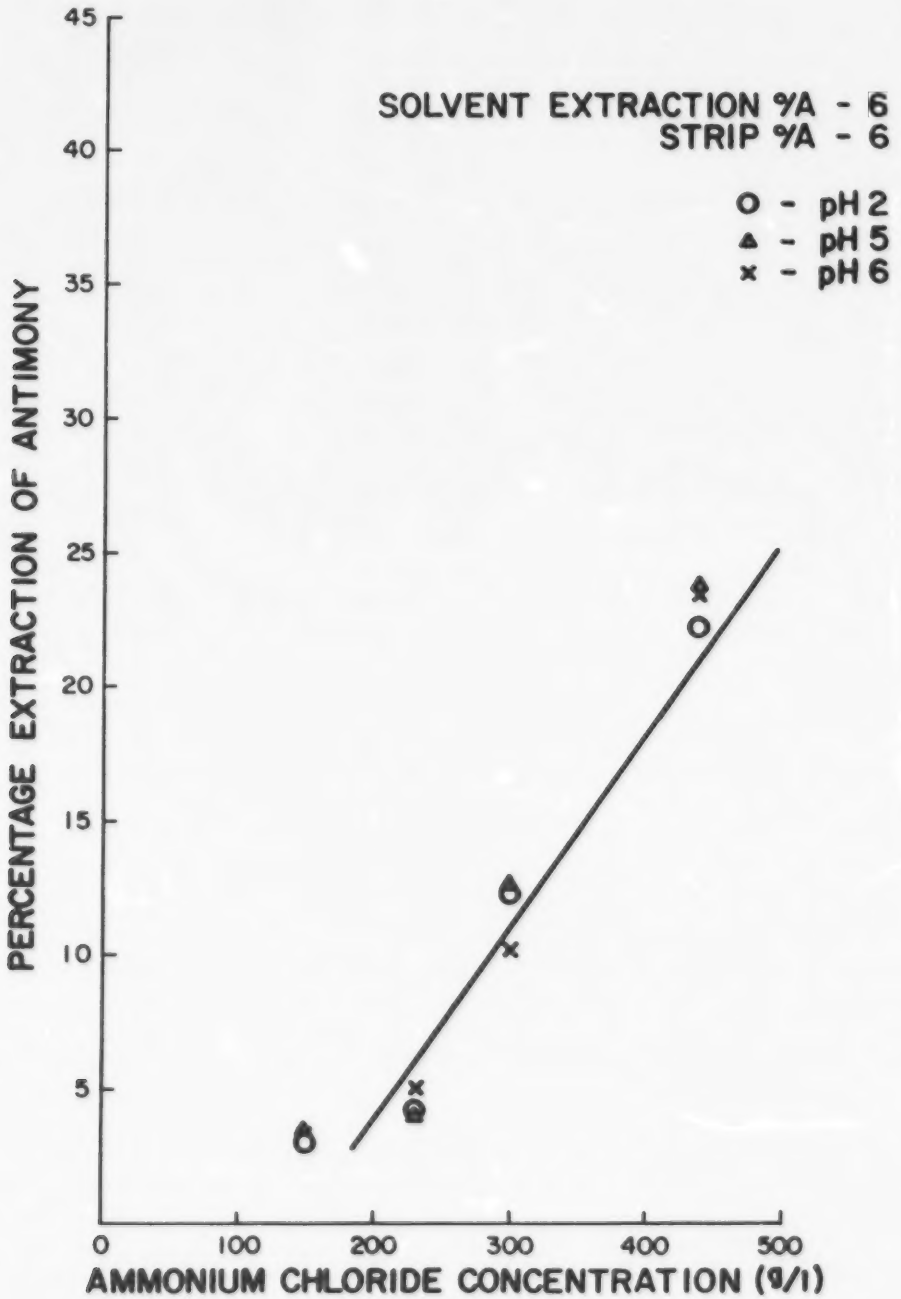


Figure 22. Stripping of Antimony (18.4 g/L Sb) from Organic Solution at Various Concentrations of Ammonium Chloride.

Table 12. Observations of Precipitate Formation with Stripping Tests

SX O/A	STRIP O/A	PH	Cl CONCENTRATION	PPT/ NO PPT	COMMENTS ON PRECIPITATE
2.4	1.3	6.5	0	ppt	large amt-white
2.4	1.3	6.5	250 g/L NaCl	ppt	small amt-white
2.4	1.3	6.5	300 g/L NaCl	ppt	cloudy
2.4	2.0	6.5	250 g/L NaCl	ppt	cloudy
2.4	1.0	6.5	250 g/L NaCl	ppt	large amt-gel
2.4	2.0	6.5	250 g/L NaCl	ppt	fluffy white
2.4	0.5	6.5	250 g/L NaCl	ppt	at interface
2.4	1.5	6.5	250 g/L NaCl	ppt	fluffy white
2.4	1.5	6.5	109 g/L HCl	ppt	large amt
2.4	1.3	6.0	230 g/L NH_4Cl	ppt	large amt-white
2.0	4.0	2.0	230 g/L NH_4Cl	ppt	
2.0	6.0	2.0	230 g/L NH_4Cl	ppt	
2.0	10.0	2.0	230 g/L NH_4Cl	ppt	
6.0	2.0	2.0	230 g/L NH_4Cl	ppt	
6.0	4.0	2.0	230 g/L NH_4Cl	ppt	
6.0	6.0	2.0	230 g/L NH_4Cl	ppt	
6.0	10.0	2.0	230 g/L NH_4Cl	ppt	
10.0	10.0	2.0	230 g/L NH_4Cl	ppt	
2.0	2.0	2.0	450 g/L NH_4Cl	no ppt	
2.0	2.0	5.0	450 g/L NH_4Cl	no ppt	
2.0	2.0	6.0	450 g/L NH_4Cl	no ppt	
6.0	6.0	2.0	450 g/L NH_4Cl	ppt	
6.0	6.0	5.0	450 g/L NH_4Cl	ppt	
6.0	6.0	6.0	450 g/L NH_4Cl	ppt	

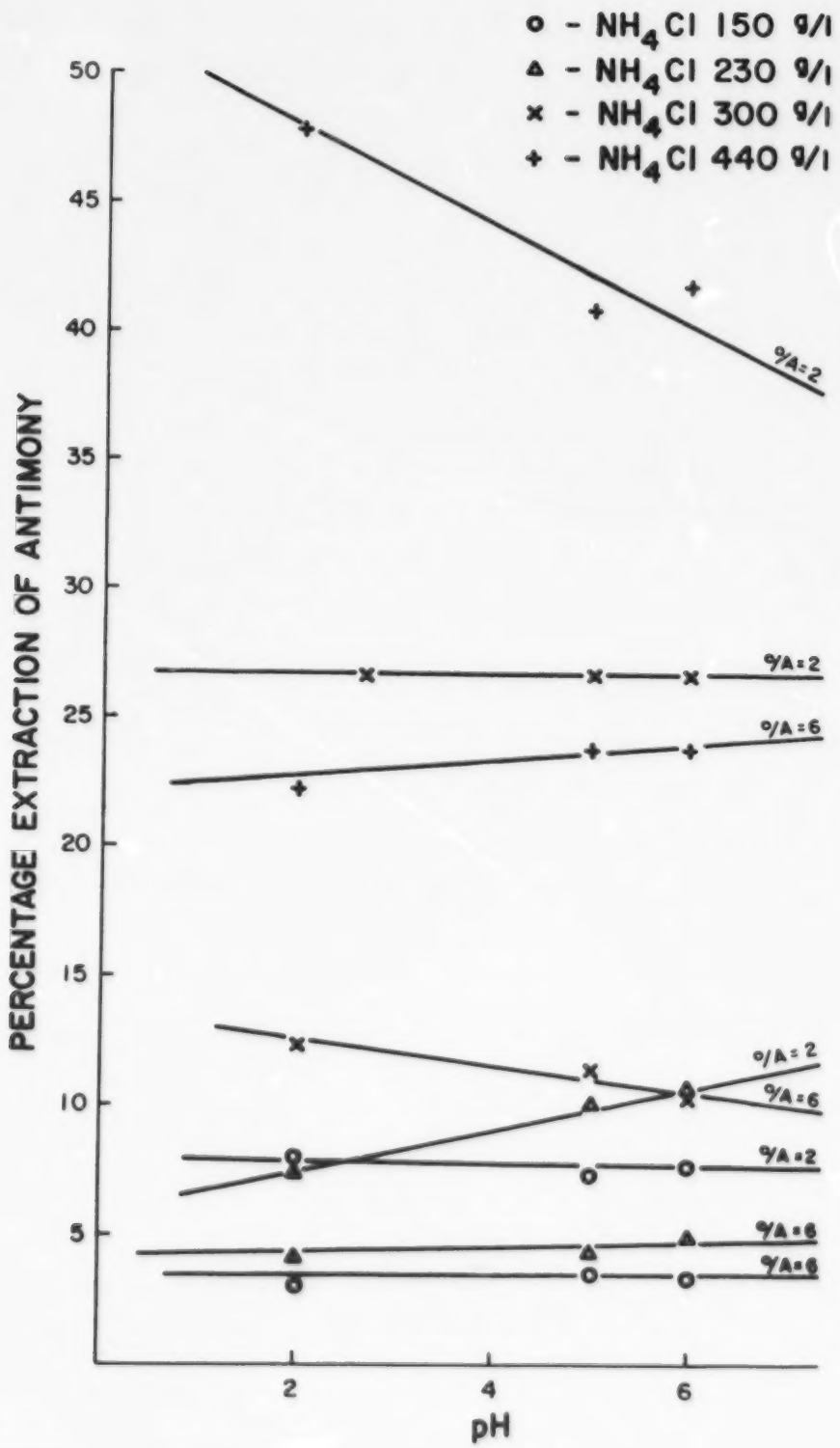


Figure 23. Stripping of Antimony (55.4 g/L Sb) from Organic Solution at Various pH Values.

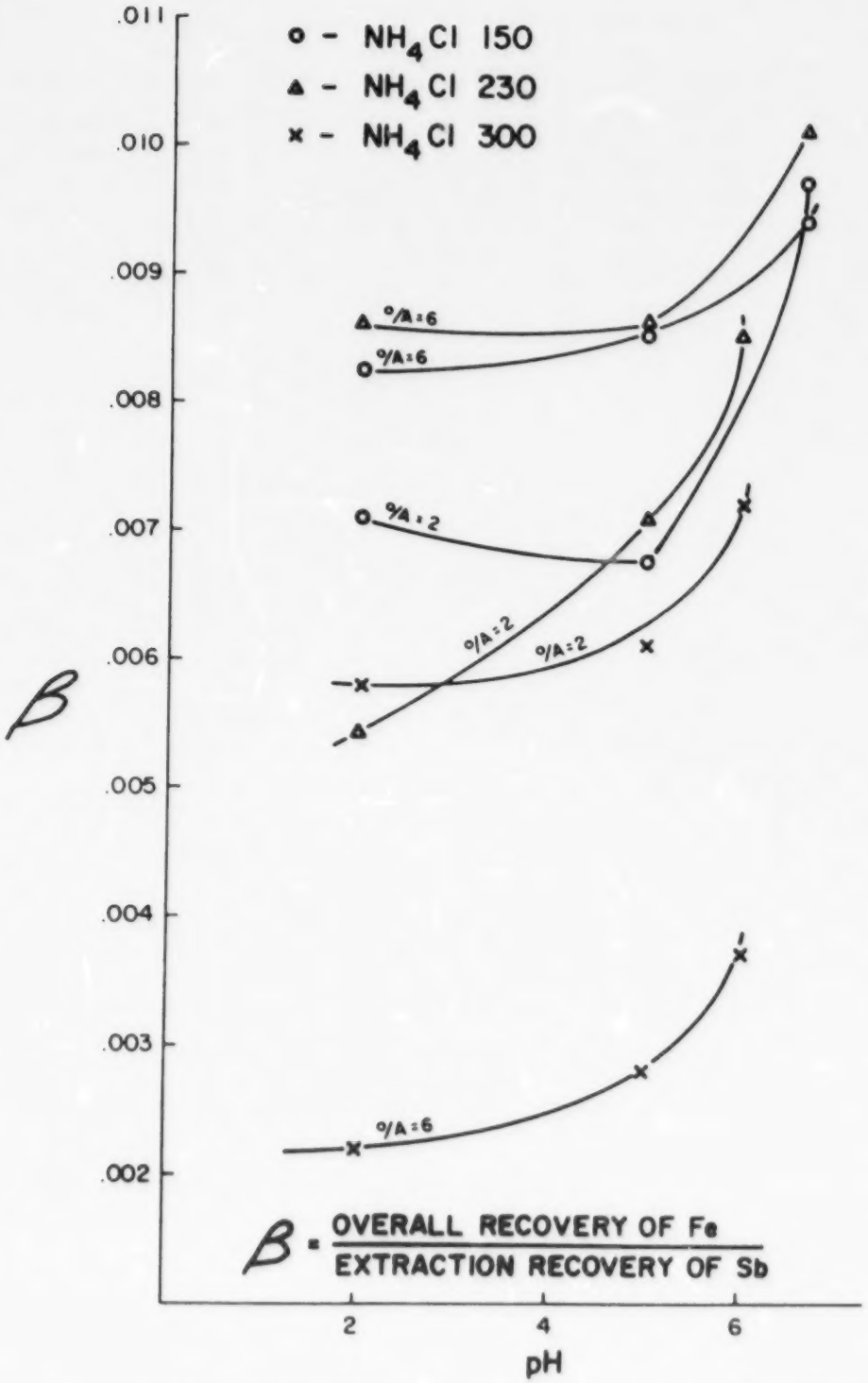
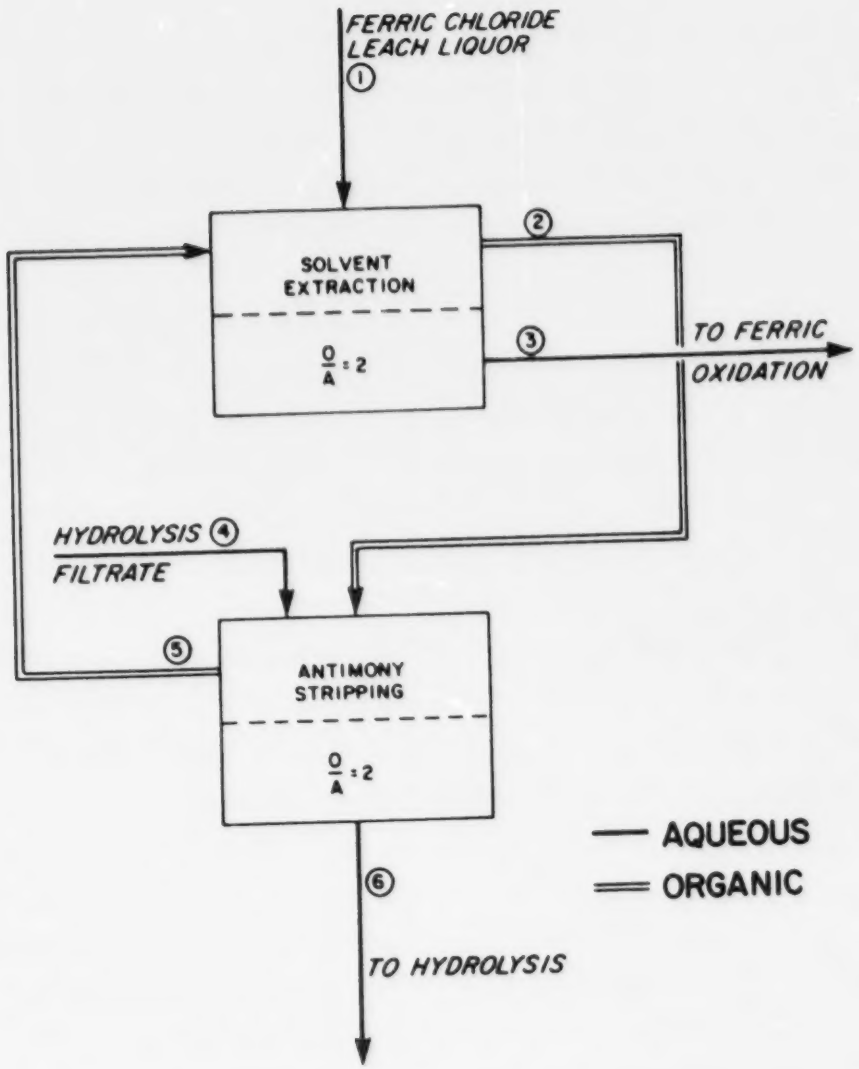


Figure 24. Selectivity of Iron and Antimony Extraction at Various Ammonium Chloride Concentrations and pH.



Stream No.	1	2	3	4*	5	6
Volume	X	2X	X	X	2X	X
Antimony Load	114	55.8	2.48	0	29.0	53.6
Antimony Weight	114X	111.6X	2.48X	0	58.0X	53.6X
Antimony Extract		97.8				48.0
Overall Extraction		47.0				

*STIP SOLUTION CONTAINING 440 gpL NH_4Cl AT pH OF 2.0
NOTE: X MEASURED IN Lt, WHERE ANTIMONY LOADING EXPRESSED IN gpL.

Figure 25. Balance of Antimony in Solvent Extraction Circuit.

aqueous solution low in chlorine (ratio of Sb:Cl is 1:2.5) which may favour oxychloride formation. In order to stabilize antimony in the strip solution a strip O/A ratio of 0.71 or less may be required. Alternatively, the concentration of antimony in the leach liquor can be reduced. At any rate, conditions of the strip will have to be designed to prevent oxychloride formation. Further test work should therefore be devoted to an understanding of antimony chloride hydrolysis.

4.3.3 Hydrolysis of Antimony Chloride

The addition of a sufficient amount of water to antimony trichloride brings about complete hydrolysis of an oxychloride compound in the form of a bulky white precipitate. The mechanism by which hydrolysis occurs with antimony cations has been reported[39] as:

$$Sb^{3+} + H_2O = (Sb(OH))^{2+} + H^+$$

in which antimony oxide may form by the decomposition of the hydroxide. The white precipitate has a tendency to absorb hydrochloric acid. The amount absorbed and the composition of the absorption product depend upon the concentration of acid in solution. In the presence of chlorine the following reaction may occur:

$$Sb^{3+} + H_2O + Cl^- = (Sb(OH)Cl)^+ + H^+$$

The absorption product has been known to alter to an oxychloride as the result of an interaction between the absorbed acid and the absorbent. The crystalline product may have different compositions depending on the equilibrium conditions within the liquid. The products of hydrolysis may have the following formulae:

$Sb_4O_3(OH)_5\ Cl$
$SbOCl$
$Sb_4O_5Cl_2$
$Sb_4O_3(OH)_3Cl_3$

Conversion between metastable states may occur as:

$$Sb_4O_3(OH)_3Cl_3 + HCl = 4SbOCl + H_2O$$
$$Sb_4O_3(OH)_3Cl_3 = Sb_4O_5Cl_2 + H_2O + HCl$$

As a result of these conversions, the hydrolysis of antimony to an oxide can be retarded by the presence of hydrochloric acid or by alkali earth chlorides.

The presence of a white precipitate occurring in SX, previously identified as oxychloride ($Sb_4O_5Cl_2$), questions the viability of producing a marketable trioxide from a chloride solution. Test work carried out using synthetic solutions of reagent grade antimony chloride according to the Occidental Petroleum Patent (Section 3.2) suggest that senarmontite production from hydrolysis is possible, and that high concentrations of antimony chloride prevents oxychloride formation. Solutions containing 8.7g $SbCl_3$/g H_2O and 3.7g $SbCl_3$/g H_2O formed trioxide hydrolysis products while 0.11g $SbCl_3$/g H_2O resulted in the formation of oxychloride. Product analysis are tabulated in Appendix IIB.

The possibility of eliminating solvent extraction from the flowsheet was reviewed. Iron and other impurities may be separated from antimony by partial hydrolysis according to the flow sheet in Figure 26. Water is added to a leach solution to selectively precipitate antimony as antimony oxychloride. The consumption of water is (Table 13) about 0.92:1 weight ratio of leach solution to water for a 99% precipitation of antimony. A metathesis was tested on the oxychloride precipitate to establish if the precipitate could be converted directly to an oxide by hydrolysis (solid-solid conversion). Conditions for hydrolysis were not changed and the product was found to contain a mixture of predominately valentinite, senarmontite and oxychloride (see Appendix IVC for analysis).

Dissolving the oxychloride precipitate in hydrochloric acid was tested at room temperature. Results are listed in Table 14. Approximately 16 tonnes of 35% HCl/tonne of oxychloride are required for dissolution. The resulting solution is very viscous and not conducive to simple solid-liquid separation. The operating cost of dissolution would be in excess of $15 per tonne of feedstock due to increased reagent and solid-liquid separation requirements. The test results indicate that solvent extraction could be replaced by partial

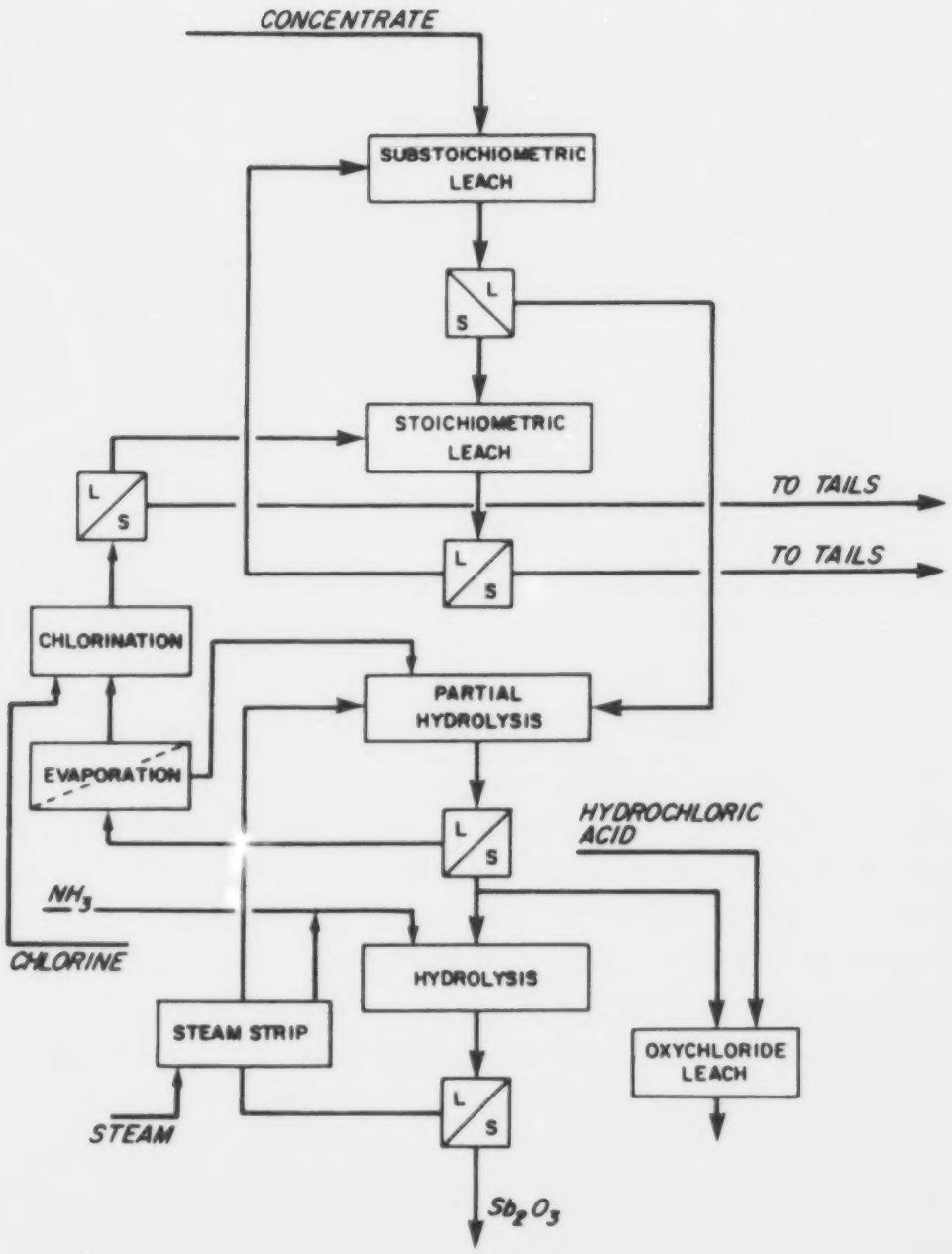


Figure 26. Process Flowsheet for Selective Precipitation of Antimony from Iron by Partial Hydrolysis.

Table 13. Water Consumption to Precipitate Oxy-Chloride

Total Volume	Water Added	pH	Sb in Solution (g/L)
92.6 mL	0 mL	.75	166.1
192.6 mL	100 mL	.30	1.0
282.6 mL	100 mL	.37	0.25
572.6 mL	300 mL	.64	0.12
1062.6 mL	500 mL	.99	0.05
1552.6 mL	500 mL	1.16	0.04
2042.6 mL	500 mL	1.23	0.02

Table 14. Hydrochloric Consumption to Dissolve Oxy-Chloride Precipitate

HCl Total	H_2O Total	pH
0 mL	20 mL	2.32
0.2 mL	20 mL	1.86
0.4 mL	20 mL	1.45
1.0 mL	20 mL	1.03
4.0 mL	20 mL	0.50
6.0 mL	30 mL	0.36
20.0 mL	30 mL	0.02
25.0 mL	30 mL	-
30.0 mL	30 mL	-
32.0 mL	30 mL	-

ppt totally dissolved.
Yellowish solution.
Quite viscous.

hydrolysis and redissolution. An oxide (Appendix IVD) containing more than 95% senomontite was produced by this method. However, the dramatic increase in operating cost does not justify the partial hydrolysis technique.

The technical feasibility of hydrolysis on strip solutions containing 53.6 g/L antimony was bench tested. At a temperature of 25°C, a chloride concentration of 0.84 g/L and a reaction time of 20 minutes, a product in excess of 95% senarmontite was produced with a yield of 98%. Product X-ray diffraction (XRD) results are listed in Appendix IVE. An additional test done at 40°C (with other conditions constant) resulted in a product containing predominately valentinite with minor amounts of senarmonite and an NH_4FeCl_3 complex (Appendix IVF). The consumption of NH_4OH, based on strip solutions of pH 2, was 2.7 Kg NH_4OH/Kg Sb (assuming the strip to contain 114 g/L Sb).

4.3.4 Production Cost

A cost analysis was prepared based on the DNRE flowsheet (Figure 15) for ferric chloride leach-SX-hydrolysis. Information generated from bench scale testing at DNRE, including reagent consumption, equipment size, and heat/power requirements, was used in costing for both operating and capital expenditures. Reagent grade chlorine gas is costed but iron and ammonium hydroxide are considered to be recycled. All calculations are outlined in Appendix III.

The major operating costs for the FCLH flowsheet are chlorine gas used for regenerating ferric chloride and heat requirements for leaching, chlorination, and steam stripping. The recycle of chlorine using an electrolysis cell to produce metal is possible. However, the recycle from hydrolysis is technically more difficult. The concept of air oxidation of ferrous chloride solutions (turbo aeration) should be technically and economically reviewed and leach reaction kinetics at lower temperatures should be reexamined.

The overall production cost of the conceptual flowsheet for ferric chloride leach-hydrolysis (FCLH) is $CDN 0.3941/lb of high purity oxide. For this process to be profitable, the price of oxide would have to exceed $US 1.70/lb (Figure 14). It is anticipated that the FCLH flowsheet is capable of producing a commercial grade antimony oxide, and the recycle of chlorine would result in a significant cost savings. It is therefore safe to say that the technology of low temperature chlorination can, with further development, become quite competitive.

4.3.5 Process Limitations

Cost comparisons suggest that FCLH processing has a lower capital cost requirement than that of a rotary kiln operation. For operating costs of FCLH to be competitive, the following process limitations must be addressed:

a) Low SX recovery of antimony from the organic phase to strip solutions. Operating conditions will have to be developed to prevent the formation of oxychloride.

b) When the SX has been optimized for Sb recovery, the selectivity of SX to separate antimony, iron, lead and arsenic should be established. To date contaminants in the product have not been identified.

c) Recycling of NH_4OH should be assessed. Assumptions have been made on recycle solution quantity and quality. The volume of recycle from hydrolysis circuit should be minimized to avoid high heat demand for ammonia flash separation.

d) The recycle of chlorine is necessary to meet economic requirements of the process. A major portion of the chloride is recycled from the SX circuit and it appears that the organic will not absorb chlorine. The possibilities of turbo aeration on recycle liquor may be feasible for regeneration of ferric solutions.

e) Leach kinetics must be developed for increased recovery of sulphur to residue.

f) Product purity is to be reviewed with respect to limiting trace valentinite and oxychloride.

4.4 Conclusions and Recommendations

The competitive nature of the antimony market makes it difficult to access commercial technology. In general, engineering firms have not become involved in developing new technology. Rather, they have concentrated on furnace design to suit conventional oxidation technology. The development of antimony processing is well established although literature on the subject has largely remained confidential.

Methods to produce antimony metal and/or oxide has traditionally focused on pyrometallurgical processing. A major problem with pyro-processing is associated with reaction kinetics and thermodynamics of oxidation, in addition to the difficulties of separating oxidized impurities. Also, combining oxidation-reduction unit operations is necessary to achieve high recoveries of marketable grade products. These operations are very capital intensive. Recent development is targeted towards processing technology designed to eliminate product impurities without multi-stage unit operations. It is expected that new development in the processing of antimony sulphides will be primarily focused on chlorination systems rather than oxygen-pyro technology.

The concept of low temperature chloride hydrometallurgy has been bench tested and indications are that such a system could be competitive. A cost analysis of conventional rotary kiln operations was used to comparatively assess the ferric chloride leach hydrolysis (FCLH) flowsheet designed and evaluated by DNRE. Major limitations were identified with solvent extraction and chlorine recycle. Advantages of the FCLH concept are in product diversification and lower capital cost.

Market demand for antimony trioxide may be prohibitive to the installation of a dedicated add-on (DRAAP) processing plant at Durham Resources Inc. The major drawback with producing antimony trioxide, which has been recognized as having the highest growth potential, is that the production tonnage (based on the Durham concentrator production tonnage) may be too high relative to market demands. Durham Resources, to be competitive in a narrowly controlled marketplace, should consider a multi-products add-

on plant. In view of this, the FCLH process, conceptualized and bench tested by DNRE, should receive serious consideration. The extended multi-product flowsheet is shown in Figure 27.

Based on this study, the following are recommended:

a) Market analysis required on marketable tonnages of various antimony compounds to determine production potential and possible sale of products (contractor estimated time and cost of six months/$15,000).

b) Development of technologies to meet various demands on antimony products based on the market study. Chloride systems may provide a competitive processing technology. An operating cost analysis will be required to compare high temperature chlorination versus low temperature systems. Further bench scale development on purification and chlorine recycle with an integrated process will be required on low temperature technology in order to assess operating costs. (Contractor estimated time and cost of nine months/$85,000).

c) Feasibility study leading to commercialization should be undertaken based on results of market and technological development. The study is to include technical processing methods, market analysis and an economic evaluation. The positive outcome of a feasibility study should lead to a pilot plant program (Contractor estimated time and cost of three months/$5,000).

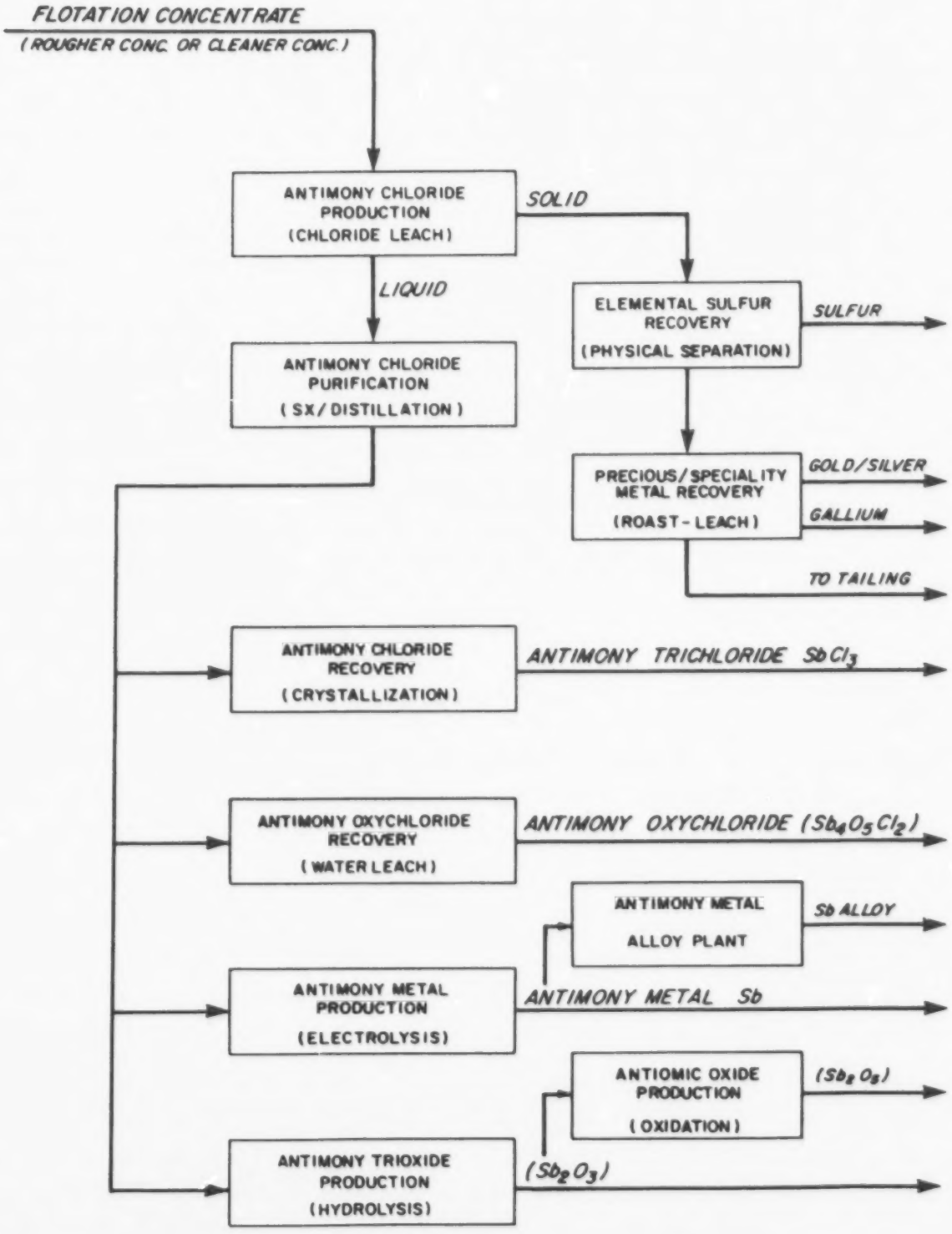


Figure 27. Conceptual Flowsheet for an Antimony Products Plant Based on a Chloride Hydromet.

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APPENDIX I

PRODUCTION OF ANTIMONY METAL BY INDUCTION FURNACE METHODS
PRELIMINARY SIZE AND COST CALCULATIONS FOR

DURHAM RESOURCES ANTIMONY PRODUCTS PLANT (DRAPP)

MARCH 1987

NOTE: Cost of equipment was based on factored costing and does not represent budget costing. Therefore costs are based on a level of confidence of plus or minus 35%. Costing has been included to establish relative comparison of technologies and to identify cost distribution.

A. Basis for Calculations

Batch Operation of Induction Furnace

Basis for Throughput:

Concentrator: $\frac{20\ t}{hr} \times \frac{24\ hr}{day} \times \frac{5\ day}{wk} \times 0.95\ avail. \times \frac{52\ wk}{yr} = 118{,}560\ \frac{t\ ore}{yr}$

Concentrate = $118{,}560 \times \frac{0.0460\ head}{0.650\ conc} \times \frac{0.87\ rec}{} = 7299.65\ \frac{t\ conc}{yr}$

Rated Capacity of DRAPP Availability = $0.95 = (1.05)^{-1}$
No. wk per yr = 52
No. day per wk = 5

Capacity: $7299.65\ \frac{t\ conc}{yr} \times 1.05 \times \frac{yr}{52\ wk} \times \frac{wk}{5\ day} \times \frac{day}{24 hr} = 1.231\ \frac{t\ conc}{hr}$
$= 29.54$ t conc/day

Cycle Time of Induction Furnace (Batch Operation)

Step 1	Addition of Dry Conc and Reagents	20 min
Step 2	Power on and Melt Charge	30 min
Step 3	Healing of Melt, Periodic Mixing	90 min
Step 4	Pour of Charge	15 min
	Total Time for Cycle	155 min (2.58 hr)

Amount of Metal Produced, Recovery of 80%

tonnage: $1.231\ \frac{t\ conc}{hr} \times 0.65\ \frac{Sb}{t\ conc} \times 0.80 = 0.64\ \frac{t\ metal}{hr}$

$= 3795.8\ \frac{t\ metal}{furnace\ yr}$

$= (32{,}156.9\ \frac{lb\ metal}{furnace\ day})$

B. Amount of Iron Required

Basis: 3 moles Fe/mole Sb_2S_3

Source of Fe: Iron oxide (iron ore), 70% Fe

Tonnage of iron ore:

$$\frac{3 \text{ mole Fe}}{\text{mole } Sb_2S_3} \times \frac{55.9 \text{ t Fe}}{\text{1 mole Fe}} \times \frac{\text{t iron ore}}{0.70 \text{ t Fe}} \times \frac{29.54 \text{ t conc}}{\text{day}} \times \frac{0.65 \text{ t Sb}}{\text{t conc}} \times \frac{339.7 \text{ t } Sb_2S_3}{243.5 \text{ t Sb}_2} \times \frac{1 \text{ mole } Sb_2S_3}{339.7 \text{ t } Sb_2S_3}$$

$$= 18.89 \frac{\text{t iron ore}}{\text{day}}$$

Cost of iron ore ($112/mt) = $2115.68/day

C. Amount of Soda Ash Required

Basis: 55% of Gangue Content by Weight

Tonnage of Soda Ash (Na_2CO_3): $0.55 \times \left(29.54 \frac{\text{t conc}}{\text{day}} - \left(29.54 \frac{\text{t conc}}{\text{day}} \times \frac{0.65 \text{ t Sb}}{\text{t conc}} \times \frac{339.7 \text{ t } Sb_2S_3}{243.5 \text{ t Sb}}\right)\right)$

$$= 1.51 \text{ t/day}$$

Cost of Soda Ash ($387/t) = $584.37/day

D. Amount of Carbon Required

Basis: 6 mole C/mole Sb_2S_3

Source of C: Coal, 95%C

Tonnage of Coal:

$$\frac{6 \text{ mole C}}{\text{mole } Sb_2S_3} \times \frac{12 \text{ t C}}{\text{mole C}} \times \frac{\text{t coal}}{0.95 \text{ t c}} \times \frac{29.54 \text{ t conc}}{\text{day}} \times \frac{0.65 \text{ t Sb}}{\text{t conc}} \times \frac{339.7 \text{ t } Sb_2S_3}{243.5 \text{ t Sb}} \times \frac{1 \text{ mole } Sb_2S_3}{339.7 \text{ t } Sb_2S_3}$$

$$= 5.98 \frac{\text{t coal}}{\text{day}}$$

Cost of Coal ($100/t) = $598/day

E. Size of Induction Furnace

Total Tonnage of Concentrate and Reagents: 18.89 t/day iron ore (34%)
1.51 t/day soda ash (3%)
5.98 t/day coal (11%)
29.54 t/day concentrate (53%)
55.92 t/day charge

Assume Use of Two Furnaces Operating in Parallel Tonnage: 27.96 $\frac{t\ charge}{day\ \ furnace}$

Tonnage Per Cycle: $27.96\ \frac{t\ charge}{day\ \ furnace} \times \frac{1\ day}{24\ hr} \times \frac{258\ hr}{cycle}$

$= 3.01\ \frac{t\ charge}{cycle}$ (6679.3 lb)

Number of Cycles Per Furnace @ 10 cycles/day/furnace

Estimated Size of Furnace for Coreless Induction Furnace: 750 kW
Cost for the Furnaces: $560,000

F. Power Requirements

NOTE: OPERATING TEMPERATURE OF 1100-1200^{O}C

Power Requirements Based on Induction Furnace Test at Sabian Manufacturing, Melt as Per Step 2 of Cycle: $120\ \frac{kW}{45.4\ kg\ conc}\ \frac{0.5\ hr}{} = \frac{1.32\ kWh}{kg\ conc}$

Heating, As Per Step 3 of Cycle: $55\ \frac{kW\cdot hr}{45.4\ kg\ conc} = 2.42\ \frac{kWh}{kg\ conc}$

Total Concentrate Per Cycle: $3.01\ \frac{t\ charge}{cycle} \times 0.53\ \frac{t\ conc}{t\ charge} \times 1000\ \frac{kg}{t}$

$= 1593$ kg/cycle

Total Power: $\left(1.32\ \frac{kWh}{kg\ conc} \times 1593\ \frac{kg\ conc}{cycle}\right) + \left(2.42\ \frac{kWh}{kg\ conc} \times 1593\ \frac{kg}{cycle}\right)$

$= 5957$ kWh/cycle

Total Power Cost: $5957\ \frac{kWh}{cycle} \times 10\ \frac{cycle}{day\ furnace} \times 2\ furnace \times \frac{\$0.05}{kWh}$

= $5957/day ($201.6/conc)

DURHAM RESOURCES ANTIMONY PRODUCT PLANT

CAPITAL COST - INDUCTION FURNACE

MARCH 1987

EQUIPMENT

Furnace with Controls and Hydraulic Lift		$ 560,000
Cooling System for Furnace		56,000
Reagent Feeding, Storage System		139,000
Furnace, Metal and Slag Removal System		20,000
	Total	775,000
Equipment Installation	(0.19)	147,250
Process Piping	(0.02)	15,500
Electrical	(0.15)	116,250
Instrumentation	(0.11)	82,250
Process Building	(0.15)	116,250
Plant Services	(0.05)	38,750
Site Improvements	(0.02)	15,500
Field Indirects	(0.02)	15,500
Project Management	(0.20)	155,000
Total Capital Investment		1,477,250
Contingency	(10%)	147,000
Subtotal		1,624,950

Note: An accuracy of 35% is equivalent to 2,194,000

( )Fraction of Equipment Cost

DURHAM RESOURCES ANTIMONY PRODUCT PLANT

OPERATING COST - INDUCTION FURNACE

MARCH 1987

Basis of 29.54 t feedstock/day, at 65% Sb, recovery 80%

Unit	Cost Per Day	Cost Per Tonne Feedstock	Cost Per Pound Metal	Distribution of Overall Cost (%)
Iron Oxide	2,116	71.64	0.0658	16.1
Soda Ash	584	19.77	0.0182	4.4
Carbon	598	20.24	0.0186	4.5
Power Required	5,957	201.66	0.1852	45.2
Manpower (9 men/$15 hr)	1,080	36.56	0.0336	8.2
Accounting/Administration	54	1.83	0.0017	0.4
Maintenance (3% of Capital)	187	6.33	0.0058	1.4
Transportation, Marketing and Insurance @ $0.02/lb saleable material	677	22.92	0.0211	5.1
TOTAL	11,253	380.94	0.3499	85.3
CAPITAL LOAN PAYMENT (11% interest, 4 years)	1,940	65.67	0.0603	14.7
SUBTOTAL	13,193	446.61	0.4102 *	100.0

* NOTE: COST DOES NOT INCLUDE THE VALUE OF CONCENTRATE

APPENDIX II

PRODUCTION OF ANTIMONY TRIOXIDE BY ROTARY KILN METHODS

PRELIMINARY SIZE AND COST CALCULATIONS FOR

DURHAM RESOURCES ANTIMONY PRODUCTS PLANT (DRAPP)

MARCH 1987

NOTE: Cost of equipment was based on factored costing and does not represent budget costing. Therefore costs are based on a level of confidence of plus or minus 35%. Costing has been included to establish relative comparison of technologies and to identify cost distribution.

A. BASIS FOR CALCULATIONS

Flowsheet Refer to Figure 5

Kiln size for 0.45 t/hr of 55% of Flotation Concentrate (Ref A1)

1.82 diameter x 7.62 length $\frac{L}{d}$ = 4.19

Flow of Air = 280 m^3/min @ 100°C = 287 kg/min

Volume of Kiln = 3.14 $(\frac{1.82}{4})^2$ x 7.62 = 19.8 m^3 (699 ft^3)

Air Stoich. based on feed tonnage = 37,333 $\frac{m^3}{t\ conc}$

= 38,323 $\frac{kg}{t\ conc}$

Deslagging: gangue forms paste after 5-6 days of operation where slag load after 5-6 days equals 8-9t slag

Require A "Burn down" cycle to

(a) maximize recovery of Sb
(b) remove slag build-up from kiln.

Feed stopped/coke added to reduce oxides to metallic form/run kiln at 1300°C using stove oil or O_2 enrichment/a fluid slag bed forms where antimony is burnt off by fuming/slag should contain less than 12% Sb/kiln is cooled where slag forms balls around 550°C and removed.

Recoveries around 93-96% with a 3% loss to slag.

Basis for Throughput:

Concentrator: $\frac{20t}{hr} \times \frac{24hr}{day} \times \frac{5day}{wk} \times 0.95\ avail. \times 52\ \frac{wk}{yr} = 118,560\ \frac{t\ ore}{yr}$

Concentrator: $118,560\ \frac{t}{yr} \times \frac{0.0460head}{0.650conc} \times 0.87rec = 7299.65\ \frac{t\ conc}{yr}$

Rated capacity of DRAPP availability = 0.90 = $(1.11)^{-1}$
no. wk per year = 52
no. day per wk = 5

Capacity: $7299.65 \frac{t\ conc}{yr} \times 1.11 \times \frac{yr}{52\ wk} \times \frac{wk}{5\ day} \times \frac{day}{24\ hr} = 1.30$ t/hr

$= 31.16$ t/day

at 95% concentrator recovery = 1.42 t/hr

$= 34.03$ t/day

DRAPP availability: assume for every 5 day of operation use 1 day for deslagging, and 90% availability

$52 \frac{wks}{yr} \times \frac{5\ day}{6\ day} \times 5 \frac{day}{wk} = 216.65 \frac{day}{yr}$ (full tonnage)

at 90% availability = $194.99 \frac{day}{yr}$ operation

tonnage: $7299.65 \frac{t\ conc}{yr} \times \frac{yr}{194.99\ day} = 37.44 \frac{t}{day}$

B. ROTARY KILN SIZE

Based on kiln size for 1.56t/hr concentrate of bulk density 2.5t/m^3. Residence time of one hour assumed

Determination of length to diameter ratio based on USBM kiln sizing

Equation, (Angle of repose 35 degrees) (1.05 RPM)

$$60 = \frac{1.77}{1.79\ D} \times \frac{\sqrt{25}}{1.05} \times \frac{L}{}$$

$$\frac{L}{D} = 4.078$$

Percentage loading in kiln is 10%

Volume of material through kiln based on bulk density: 0.62 m^3/hr.

For 1 hour residence time size of kiln = $\frac{0.62}{0.10} \times 1 \times \frac{35.29}{m^3}\ ft^3$

$= 219.56\ ft^3$

Volume = $\frac{3.14}{4} d^2 (4.7\ d) = 219.56\ ft^3$

$d = 3.89$ ft

C. RECOVERY OF OXIDE

Slag build up of $\frac{8\ t\ slag}{5\ day\ operation} \times 0.12\ \frac{Sb}{slag} = 0.19\ \frac{t\ Sb}{day}$

amount of Sb in feed = $10.8\ \frac{conc}{day} \times 0.55 = 5.94$ t conc/day

Recovery (max.) = $\frac{5.94 - 0.19}{5.94} \times 100\% = 96.8\%$

Based on assays (82% Sb for Sb_2O_3 concentrate)

Two product formula = $\frac{55 - 12}{82 - 12} \times \frac{82}{55} = 91.6\%$

Recovery in the range of 91.6 - 96.8%

D. AIR REQUIREMENTS

Based on Ref # A1

Total volume of air for cooling and oxidation:

$37,333\ \frac{m^3}{t\ conc} \times 31.16\ \frac{t\ conc}{day} = 1,163,296\ \frac{m^3}{day}$

by stoichiometry of

$2Sb_2S_3 + 9O_2 = 2Sb_2O_3 + 6SO_2 + 68.57$ Kcal

Volume of air for oxidation: $31.16\ \frac{t\ conc}{day} \times 0.65\ \frac{Sb}{t\ conc} \times \frac{1\ t\ Sb_2S_3}{0.71\ Sb} \times \frac{1\ mole\ Sb_2S_3}{339.69\ t\ Sb_2S_3}$

$\times \frac{9\ mole\ O_2}{2\ mole\ Sb_2S_3} \times \frac{32\ t\ O_2}{mole\ O_2} \times \frac{1\ t\ air}{0.23 t O_2} \times \frac{1000\ kg}{t}$

$\times \frac{m^3\ (STP)}{1\ kg}$

$= 52,578\ \frac{m^3}{day}$ (4.5% of total air required)

$= 2190.75 \frac{kg}{hr}$

E. HEAT REQUIREMENTS

Basis of 68.57Kcal/g. mole Sb_2S_3 from oxidation reaction, Reference A1.

Heat generated from reaction: $1.30 \frac{t}{hr} \frac{conc}{t\ conc} \times 0.92 \frac{t\ Sb_2S_3}{} \times 1000 \frac{kg}{kg} \times 1000 \frac{g}{kg}$

$$\frac{1\ mole\ Sb_2S_3}{339.69\ gm} \times 68.57 \frac{K\ cal}{2\ g\,mole\ Sb_2S_3}$$

$$= 120{,}958\ Kcal/hr$$

$$= 498{,}348\ Kjoule/hr$$

Heat required for process (air)

$Q = mCp\ T_{Kiln}$ Tin = 25° Tout = 1200°C

$$= 2190.75 \frac{kg}{hr} \times \frac{1kJ}{kg^{\circ}C} (1075^{\circ}C)$$

$$= 2{,}355{,}056 \frac{kJ}{hr}$$

Additional fuel required = $2{,}355.056 - 498{,}348 \frac{kJ}{hr}$

$$= 1{,}856{,}708 \frac{kJ}{hr}$$

$$= (1.86\ mm\ BTU/hr)$$

For a turn down of 21% = $2.35\ mm \frac{BTU}{hr}$ heat required from burner

Note: Assumption on heat loss and heat contained by solids.

Assume heat loss of 7% total heat required and a thermal efficiency of 85% (Perry 20 - 36)

Net fuel requirements: $\frac{1.86\ mm\ BTU}{(0.65 - 0.07)} = (3.21\ mm \frac{BTU}{hr})$

Fuel requirements for norm operation:

No. 6 fuel oil: $6{,}000 \frac{BTU}{lb}$

How rate: 3.21 mm $\frac{BTU}{hr}$ × $\frac{}{6{,}000\ BTU}$ × $\frac{4.5392.10^{-14}\ mt}{lb}$ × $\frac{m^3}{0.876\ mt}$ × $1000\ \frac{L}{m^3}$

$= 276.95\ \frac{L}{hr}$

at $0.259 per L

Fuel cost = $276.95\ \frac{L}{hr} \times \$0.259 \times \frac{24\ hr}{day}$

= $1721 per day

($55/tonne feedstock)

F. ESTIMATED KILN COST

Factored costing based on 200 -500 mtpd units having 1 hour residence time.

Cost includes feeding system, controls, motor, liner

for 40 mt/day, Purchase cost.....$512,000
Installation cost..... 384,000

Total cost..... 896,000

G. FEED HOPPER

Basis of feed to DRAPP = 37.44t/day max

Bulk density 2.5 $\frac{tonne}{m^3}$

Note: Bin design to have 2 day surge capacity from concentrator to allow for deslagging time on kiln and availability

Bin volume: 2 day × $37.44\ \frac{t}{day} \times \frac{m^3}{2.5\ t} = 29.95\ m^3$

Carbon steel bin 30 m^3.....$24,000

Apron feeder 8' x 24" 3 Hp.....11,000

Installation.....10,000

Total.....$45,000

H. COOLING SECTION, SUBLIMATION UNIT

Heat in gas stream = heat removed by cooling pipes

Heat transfer area = outside area of pipe (πdL)

$$mCp\ T_i = hA\ T_o$$

h: combined heat transfer coefficient for convection and radiant heat loss.
A: π (diameter of pipe)(length of pipe).
To: wall temperature and ambient temperature.
Ti: gas temperature from kiln and to bag house

From figure 2.5:

temperature of gas from kiln: 1200°C (2192°F)
temperature of gas from quinch shroud: 800°C (1472°F)
temperature of gas from secondary cooling pipes: 250°C (482°F)

Mass flow of air from rotary kiln and quinch shroud: 48,471 Kg/hr (22,000 lb/hr)

Amount of heat given off by gas cooling

$$Q = 22{,}000\ lb/hr \times 0.29\ BTU/lb\ ^oF\ (1472 - 482^oF)$$

$$= 6.32 \times 10^6\ BTU/hr$$

Radiant heat transfer coefficient (Emissivity for nickel-chrome steel)

$$hr = \frac{1.322 \times 10^{-16}\ BTU/ft\ .h.R^4\ (0.70) \times (1932^4 - 532^4)}{(1932 - 532\ ^oR)}$$

$$= 9.1564 \times 10^{-7}\ BTU/ft^2.h\ ^oR$$

Convection heat transfer coefficient

From J. P. Holman 4th Ed. HEAT TRANSFER (page 253)

Simplified equations for air...
Free convection from a vertical cylinder, laminar airflow

$$h = 1.42 \left(\frac{To}{d}\right)^{0.25},\ w/m^2\ ^oC$$

$$To = Tw - Too\ ,\ ^oC$$

vertical dimension, m

For pipes at 0.306m (12 inches) Tw ~ 525°C on average

$$h = 1.42 \left(\frac{500}{0.306}\right)^{0.25}$$

$$= 9.0296 \ W/m^{2}{}^{\circ}C$$

$$= 1.699 \ BTU/hr\ ft^{2}{}^{\circ}F$$

Diameter of pipe calculation

$$Q = h(\pi dL)\ To$$

$$L = \frac{Q}{h\pi d^{2}\ To}$$

$$= \frac{6.32 \times 10^{6}}{1.699\ (3.14)(1\ ft.)^{2}(977)}$$

$$\sim 1200\ ft$$

At a height of 40ft number of tubes is approximately 30

Estimate for 12" stainless steel pipe 316L at $175 per foot.....$210,000
Installation cost at 25% of purchase cost.....$ 52,500
Engineering design and management 25% of purchase cost.....$ 52,500

TOTAL COST.....$315,000

I. DUST COLLECTION AND PRODUCT PACKAGING

(Ref: H. S. Peters pg. 599)

For a gas flow of 48,471 m^3/hr (28,509 ft^3/min).....$150,000

Product packaging unit..... 30,000
Installation..... 45,000

TOTAL.....$225,000

J. FLUE GAS SCRUBBING

(Ref: H. S. Peters g. 598)

Venturi scrubber for 28,509 ft^3/min gas.....$ 55,800

stack (100 ft) pipe.....$ 10,580

ID fan and backup.....$ 18,600

Installation.....$ 21,000

Total.....$106,000

Reagent cost for scrubber using lime (for 70-80% removal of sulfur oxide).

sulphur emission: $31.16 \frac{t \text{ conc}}{day} \times 0.65 \frac{Sb}{\text{conc}} \times \frac{339.69 \ Sb_2S_3}{243.50 \ Sb_2} \times \frac{96.19 \ S_3}{339.69 \ Sb_2S_3}$

$\times 1.5 \frac{t \ SO_2}{ts}$

$= 12 \frac{t \ SO_2}{day}$

For lime with effectiveness factor of 0.65

amount CaO: $1 \frac{\text{mole CaO}}{\text{mole } SO_2} \times 1 \frac{\text{mole } SO_2}{48 \text{ t } SO_2} \times 12 \text{ t } SO_2 \times 56.08 \frac{t \text{ CaO}}{\text{mole CaO}} \times (0.65)^{-1}$

= 21.57 t CaO/day

cost: at $25/tonne $\times$ 21.57 $\frac{t \text{ CaO}}{day}$ = $539.25/day

K. POWER REQUIREMENTS

Rotary Kiln (50 hp), Kiln Feeder (5 Hp), Air Fans (2x3 Hp), Pumps (6x2 Hp)

73 Hp (at $0.05/KWh) $67.10/day

L. MANPOWER - LABOUR

3 men per shift, 3 shift/day, 8 hr shift, $15/hr (5 day week) = $1080/day

M. PRODUCTION/REVENUE

Tonnage of trioxide: $31.16 \frac{t\ conc}{day} \times 0.65 \frac{Sb}{conc} \times 0.92\ Rec \times \frac{Sb_2O_3}{0.7168 Sb_2} = 26.0 \frac{t\ Sb_2O_3}{day}$

$= 57,269 \frac{lb\ Sb_2O_3}{day}$

Revenue value of \$1.50/lb) = \$85,904/day

Annual revenue: where availability = 90%
non-deslagging time = 83%
5 day a week operation

$\frac{\$85,904}{day} \times 5 \frac{day}{wk} \times 52 \frac{wk}{yr} \times 0.90\ avail. \times 0.83\ op$

= \$16,684,274/yr

DURHAM RESOURCES ANTIMONY PRODUCT PLANT

CAPITAL COST - ROTARY KILN METHODS

MARCH 1987

EQUIPMENT & INSTALLATION

Kiln Feed Hopper and Feed System (automated)		$ 45,000
Rotary Kiln		896,000
Quench, primary and secondary cooling unit		315,000
Exit gas baghouse and packaging		225,000
Sulphur dioxide scrubber unit, stack, induced draft fan		106,000
	Total	1,587,000
Process Piping	(0.10)	159,000
Electrical	(0.25)	397,000
Instrumentation	(0.11)	175,000
Process Building	(0.10)	159,000
Plant Services	(0.05)	79,000
Site Improvements	(0.02)	32,000
Field Indirects	(0.02)	32,000
Project Management	(0.20)	317,000
Total Capital Investment		2,937,000
Contingency	(10%)	294,000
Subtotal		3,231,000

Note: An accuracy of 35% is equivalent to 4,362,000

( )Fraction of Equipment Cost

DURHAM RESOURCES ANTIMONY PRODUCT PLANT

OPERATING COST - ROTARY KILN METHODS

MARCH 1987

Basis of 31.16 t feedstock/day, at 65% Sb, min recovery 92%

Unit	Cost Per Day	Cost Per Tonne Feedstock	Cost Per Pound Oxide	Distribution of Overall Cost (%)
Fuel (#6) for Kiln Heat	1,721	55.23	0.0301	19.1
Reagent for Scrubber	539	17.30	0.0094	5.9
Power Requirements	67	2.15	0.0012	1.3
Manpower (9 men/$15 per hour)	1,080	34.66	0.0189	11.9
Accounting/Administration	54	1.73	0.0009	0.6
Maintenance (3% of Fixed Capital)	286	9.18	0.0050	3.2
Transportation, Marketing and Insurance @ $0.02/lb saleable material	1,145	36.74	0.0200	12.7
TOTAL	4,892	157.00	0.0855	54.7
Capital Loan Payment (11% interest, 4 years)	3,854	123.69	0.0714	45.3
SUBTOTAL	8,746	280.69	0.1569 *	100.0

* Note: Cost does not include the value of concentrate.

APPENDIX III

PRODUCTION OF ANTIMONY TRIOXIDE BY FERRIC CHLORIDE LEACH - HYDROLYSIS METHOD

PRELIMINARY SIZE AND COST CALCULATIONS FOR

DURHAM RESOURCES ANTIMONY PRODUCTS PLANT (DRAPP)

MARCH 1987

NOTE: Cost of equipment was based on factored costing and does not represent budget costing. Therefore costs are based on a level of confidence of plus or minus 35%. Costing has been included to establish relative comparison of technologies and to identify cost distibution.

A. Basis for Calculations

Flowsheet refer to Figure 15

Capacity: Base on 31.16 t/day of flotation concentrate at 65% Sb.

Availability: 5 day/wk operation
90% availability

$$52 \frac{wk}{yr} \times 5 \frac{day}{wk} \times 0.90 \text{ avail} = 234 \frac{day}{yr} \text{ operation}$$

$$\text{Tonnage: } 31.16 \frac{t}{day} \times 52 \frac{wk}{yr} \times 5 \frac{day}{wk} \times \frac{yr}{234\ day} = 34.62 \frac{t\ conc}{day}$$

Note: For leach plant concentrate should be dewatered to 50-60% solids and drying of concentrate will not be required. The oxide produced from this process will have to be dried, therefore drying cost assumed to be similar to cost of drying concentrate from flotation circuit.

This cost analysis has been done on a conceptual flowsheet where optimum residence times and solution volumes and solution densities have been based on preliminary work done in lab.

Plastic tanks have been selected for hydromet have been costed on factored quotes from manufactures.

Assume overall recovery for process 92%.

B. Substoichiometric Leach

Leach percentage solids: 15% solids sp. gr. 4.0.

slurry sp. gr. 1.13 t/m^3

Require 3 tanks with residence time of 2 hr. each

$$\text{Volume of tank} = 34.62 \frac{ts}{day} \times \frac{1\ day}{24\ hr} \times \frac{m^3}{1.13\ t} \times \frac{t\ slurry}{0.15\ ts} \times 2\ hr = 17.02\ m^3$$

Total cost of 3 tanks with agitators.....$55,000

Thickener for solid/liquid separation, assume 7 m diameter complete with rake mechanism & motor.....$30,000

Total cost of equipment.....$85,000

C. Stoichiometric Leach

Size of leach circuit similar to subst. leach, for three tanks/agitator and thickener.

Total cost of equipment.....$85,000

D. Solvent Extraction

Volume of leach soln = 34.62 $\frac{t \text{ solids}}{day} \times \frac{1 \text{ day}}{24 \text{ hr}} \times \frac{m^3}{1.13 \text{ t}} \times \frac{t \text{ slurry}}{0.15 \text{ t solid}}$

= 8.51 m^3/hr

Volume of organic based on 2:1, organic:aqueous = 17.02 m^3/hr

Volume of SX units having 10 min retention time = 17.02 $\frac{m^3}{hr} \times 10 \text{ min} \times \frac{1 \text{ hr}}{60 \text{ min}}$

for cell with agitator cost.....$ 4,000

Estimate 2 cells for extraction and 5 cells for strip.....$28,000

E. Antimony Hydrolysis

Require 3 tanks with 30 min residence time

Tank volume: 8.51 $\frac{m^3}{hr} \times 0.50 \text{ hr} = 4.3 \text{ m}^3$

Cost for 3 tanks with agitator.....$15,000

Thickener for hydrolysis product (7 m dia with rake).....$30,000

Drum filter for hydrolysis product

Tonnage of trioxide: 34.62 $\frac{t \text{ conc}}{day} \times 0.65 \frac{Sb}{conc} \times 0.92 \text{ rec} \times \frac{Sb_2O_3}{0.7168} = 28.88 \frac{t \ Sb_2O_3}{day}$

= 1.20 t/hr @ 50% solids

Flowrate of filtrate = 1.20 t/hr soln $\times \frac{m^3}{1.09 \text{ t}}$

= 1.10 m^3/hr (35.3 ft^3/hr)

For a drum filter of 11 m^2 filtration area....$120,000

Total equipment for hydrolysis.....$165,000

Reagent cost for hydrolysis based on 2.7 kg NH_4OH/kg Sb

Amount of Sb in hydrolysis soln = 34.62 $\frac{t \text{ conc}}{day}$ x 0.65 $\frac{t \text{ Sb}}{t \text{ conc}}$ x 0.92 rec

Cost of NH_4OH assuming 5% of total requirements used in make-up (NH_4OH @ $0.298/kg)

20.7 $\frac{t \text{ Sb}}{day}$ x 2.7 kg $\frac{NH_4OH}{kg \text{ Sb}}$ x $\frac{1000 \text{ kg Sb}}{t \text{Sb}}$ x $\frac{0.298}{kg \text{ } NH_4OH}$ x $\frac{0.05 \text{ day}}{34.62 \text{ t conc}}$

= $24.06/tonne conc.

F. Ferric Chlorination

3 tanks required with 2 hr retention time

Volume of soln. approximately 8.51 m^3/hr

Volume of tank: 2 hr x 8.51 $\frac{m^3}{hr}$ = 17 m^3

for 3 tanks 316 SS with agitation mechanisms..$ 45,000
thickener for ferric hydroxide (3 m).....$ 16,000

Cost of chlorine based on stoichiometry

$FeCl_2 + 1/2\ Cl_2 = FeCl_3$

For leach stoichiometric requirements are 6 mole $FeCl_3$/mole Sb_2S_3

$6FeCl_3 + Sb_2S_3 = 6FeCl_2 + 2SbCl_3 + S_3$

Weight ratio: 0.625 $\frac{g \text{ Sb}}{g \text{ conc}}$ x $\frac{338.69 \text{ g } Sb_2S_3}{243.50 \text{ g } Sb_2}$ x $\frac{1 \text{ mole } Sb_2S_3}{338.69 \text{ g } Sb_2S_3}$ x $\frac{6 \text{ mole } FeCl_3}{\text{mole } Sb_2S_3}$

x 162.2 $\frac{g \text{ } FeCl_3}{\text{mole } FeCl_3}$

= 2.50 g $FeCl_3$/g conc

Tonnage of oxidant: 34.62 $\frac{t \text{ conc}}{day}$ x 2.50 $\frac{t \text{ } FeCl_3}{t \text{ conc}}$ = 86.55 $\frac{t \text{ } FeCl_3}{day}$

Tonnage of chlorine: $\frac{0.5 \text{ mole } Cl_2}{\text{mole } FeCl_3} \times \frac{1 \text{ mole } FeCl_3}{162.2 \text{ t } FeCl_3} \times \frac{85.55 \text{ t } FeCl_3}{\text{day}} \times \frac{70.8 \text{ t}}{1 \text{ mole } Cl_2}$

$= 18.67 \frac{\text{t } Cl_2}{\text{day}}$

Cost ($0.05/kg) = $18.67 \frac{\text{t } Cl_2}{\text{day}} \times \frac{1000 \text{ kg}}{\text{t}} \times \frac{\$0.65}{\text{kg}} \times \frac{\text{day}}{34.62 \text{ t conc}}$

$= \frac{\$350.56}{\text{t conc}}$

Total cost equipment.....$ 61,000

G. Steam Strip

		Feed	Overhead	Bottom
Basis:	Mass Fraction of NH_4	0.25	0.95	0.10
	Heat content (BTU/lb)	25	695	90
	Flow (lb/hr)	18,000	3,000	15,000

From heat and mass balance, amount of heat to flash $NH_3 = 3.3 \times 10^6 \frac{\text{BTU}}{\text{hr}}$

Size heat exchanger: Q=UA T

$$A = \frac{Q}{U\ T} = 3.3 \times 10^6 \frac{\text{BTU}}{\text{hr}} \times \frac{\text{hr ft}^2 {}^\circ\text{F}}{400 \text{ BTU}} \times \frac{1}{216 {}^\circ\text{F}}$$

$= 38.2 \text{ ft}^2$

Cost for double pipe heat exchanger 316 SS.....$ 6,000

Flash tank (retention time 10 min.)

$V = 10 \text{ min} \times \frac{1 \text{ hr}}{60 \text{ min}} \times 8.51 \frac{\text{m}^3}{\text{hr}} = 1.42 \text{ m}^3$

Flash tank.....$ 3,000

Total cost steam strip equipment.....$ 9,000

H. Heat Requirements

Heat required for leach output circuit at 85°C 2.20 x 10^6 BTU/hr

Heat required for chlorination at 85°C 2.3 x 10^6 BTU/hr

Heat required for steam strip 3.3 x 10^6 BTU/hr

Total 7.8 x 10^6 BTU/hr

Assume a heating efficiency of 75%, heat require = 10.0 x 10^6 BTU/hr

Boiler required for heat demand.....$70,000

Oil requirements (#6 fuel oil): $10.0 \times 10^6 \frac{BTU}{hr} \times \frac{lb}{6{,}000\ BTU} \times 0.52 \frac{L}{lb} = 853.62 \frac{L}{hr}$

Cost per day: $863.62 \frac{L}{hr} \times \frac{\$0.259}{L} \times 24 \frac{hr}{day} = \$5368.28$

I. Pump Requirements

Require approximately 37 pumps rated at 10 m^3/hr

Total cost for centrifugal rubber lined (37 g/m).....$200,000

J. Manpower - Labour

3 men per shift, 3 shift/day, 8 hr shift, $15/hr
(5 day/wk.....$ 1,080/day

K. Power Requirements

40 motors @ 3 Hp.....(@ 0.05/kWh) .....$ 116.28/day

L. Production/Revenue

Tonnage of trioxide:

$$31.16 \frac{t\ conc}{day} \times 0.65 \frac{Sb}{conc} \times 0.92\ rec \times \frac{Sb_2O_3}{0.7168\ Sb_2} = 26.0 \frac{t\ Sb_2O_3}{day}$$

$$= 57{,}269 \frac{lb\ Sb_2O_3}{day}$$

at $1.50/lb Revenue of.....$85,904/day

Annual revenue:

where availability = 90%
t day/wk operation

$$\frac{\$85,904}{\text{day}} \times 5\ \frac{\text{day}}{\text{wk}} \times 52\ \frac{\text{wk}}{\text{yr}} \times 0.90\ \text{avail}$$

$$= \$20,101,536/\text{yr}$$

DURHAM RESOURCES ANTIMONY PRODUCT PLANT

CAPITAL COST - FERRIC CHLORIDE LEACH - HYDROLYSIS METHODS

MARCH 1987

EQUIPMENT

Leach Circuit and Dewatering		$ 170,000
Solvent Extraction		32,000
Hydrolysis Reactor and Dewatering		165,000
Ferric Chlorination		61,000
Steam Strip		9,000
Utilities (boiler, pumps)		270,000
Total		707,000
Equipment Installation	(0.25)	177,000
Process Piping	(0.30)	212,000
Electrical	(0.32)	226,000
Instrumentation	(0.23)	163,000
Process Building	(0.10)	71,000
Plant Services	(0.05)	35,000
Site Improvements	(0.02)	14,000
Field Indirects	(0.02)	14,000
Project Management	(0.20)	141,000
Total Capital Investment		1,760,000
Contingency	(10%)	176,000
Subtotal		1,936,000

Note: An accuracy of plus 35% is equivalent to $2,614,000

( )Fraction of Equipment Cost

DURHAM RESOURCES ANTIMONY PRODUCT PLANT

OPERATING COST - FERRIC CHLORINE LEACH - HYDROLYSIS METHOD

MARCH 1987

Basis of 31.16 t feedstock/day, at 65% Sb, min recovery 92%

Unit	Cost Per Day	Cost Per Tonne Feedstock	Cost Per Pound Oxide	Distribution of Overall Cost(%)
Chlorine Gas ($0.65/kg)	12,136.00	389.49	0.2119	53.8
Ammonium Hydroxide ($0.298/kg)	832.95	26.73	0.0145	3.7
Fuel For Heat Demand (#6 Fuel Oil	5,368.28	172.28	0.0938	23.8
Power Requirements ($0.05/kWh)	116.28	3.73	0.0020	0.5
Manpower	1,080.00	34.65	0.0189	4.7
Accounting/Administration	54.00	1.73	0.0009	0.2
Maintenance (3% of Fixed Capital)	125.78	40.36	0.0022	0.6
Transportation, Marketing and Insurance @ $0.02/lb saleable material	1,145.00	36.74	0.0200	5.1
TOTAL	15,490	497.11	0.2705	92.4
Capital Loan Payment (11% interest, 4 years)	2,309	74.10	0.04033	7.6
SUBTOTAL	17,799	571.21	0.3108 *	100.0

* Note: Cost does not include the value of concentrate.

APPENDIX IV

X-RAY DIFFRACTION ANALYSIS OF VARIOUS COMPOUNDS PRODUCED BY THE FERRIC CHLORIDE LEACH-HYDROLYSIS FLOWSHEET.

(ANALYSIS DONE BY RESEARCH AND PRODUCTIVITY COUNCIL M86/037)

Appendix IVA: Complex formed in strip solutions

Oxychloride Valentinite approx. 6%

(Sb_2O_3 - 2SbOCL) approx. 30%

Smear

Intensities	D-Spacings	Possible Identification
51	6.204	6.19 (50) B
4	4.787896	4.78 (12) B
3	4.600293	4.571 (18) Val.
6	4.074684	4.07 (30) B
2	3.947802	3.942. (6) B
3	3.879485	3.867 (10) B
12	3.705183	3.703 (35) B
3	3.525072	3.494 (25) Val. 3.525 (12) B
2	3.370700	3.368 (6) B 3.352 (3) B
30	3.283408	3.286 (100) B
6	3.145140	3.142 (100) Val.
16	3.118566	3.118 (75) Val. 3.126 (85) B
21	3.086031	3.095 (10) B
5	2.848482	2.848 (8) B
3	2.807802	2.808 (8) B
8	2.648907	2.650 (13) Val. 2.653 (10) B
17	2.557136	2.559 (45) B
5	2.513749	2.511 (16) B
31	2.391533	2.396 (5) B
2	2.379193	2.370 (3) Val.? 2.388 (6) B 2.377 (4) B
2	2.268954	2.263 (6) B
4	2.147846	2.196 (3) B
4	2.135208	2.146 (10) B 2.132 (10) B
18	2.061097	2.063 (10) B
8	2.051448	2.059 (9) Val. 2.050 (30) B
2	1.997001	2.016 (5) B
4	1.974355	1.9961 (3) B 1.99779 (8) B 1.9718 (5) B
2	1.931725	1.9288 (11) Val
2	1.866623	
3	1.853612	
2	1.819729	
1	1.806629	1.8046 (20) Val.
3	1,784827	
2	1.753509	
2	1.680236	1.6745 (9) Val.
2	1.653056	
3	1,643492	
2	1,625621	
2	1,606960	
1	1,596383	
3	1,572356	

B: Sb_2I_3-2SbOCl ASTM 30-91A

Appendix IVB: Hydrolysis Production from Synthetic $SbCl_3$ Solution

Senarmontite (Sb_2O_3) plus 90%

Minor Valentinite

Pellet

Intensities	D-Spacing	Possible Identification
90+	6.345	6.44 (12) Sen.
33	4.564	4.571 (18) Val.?
3	3.551	
4	3.493	3.494 (25) Val.
90++	3.180	3.218 (100) Sen., 3.142 (100) Val., 3.118 (75) Val.
25	2.778	2.788 (40) Sen.
6	2.705	2.738 (9) Val., 2.712 (4) Val.
3	2.644	2.650 (13) Val.
13	2.555	2.559 (11) Sen.
8	2.457	2.456 (4) Val.
2	2.272	2.276 (2) Sen., 2.271 (3) Val.?
4	2.142	2.145 (3) Sen.
37	1.966	1.972 (42) Sen., 19288 (11) Val.?
2	1.803	1,8046 (20) Val.
19	1.678	1.681 (35) Sen., 1.6745 (9) Val.
22	1.607	1.611 (11) Sen.
6	1.562	1.562 (7) Sen.
28	1.523	1.5226 (11) Val.

Appendix IVC: Hydrolysis Product of Oxychloride Hydroysis (Metathesis)

Senarmontite (Sb_2O_3) plus 90%

Minor Valentinite

Pellet

Intensities	D-Spacing	Possible Identification
4	6.174849	6.19 (50) B
5	4.562166	4.571 (18) Val. 4.78 (12) B
4	4.055824	4.07 (30) B
2	3.848335	3.942 (6) B, 3.867 (10) B
5	3.69095	3.703 (35) B
7	3.48913	3.494 (25) Val., 3.525 (12) B
2	3.3537	3.368 (6) B, 3.357 (3) B
12	3.27735	3.286 (100) B
4	3.20838	3.218 (100) Sen.?? 3.174 (20) Val.
31	3.121336	3.142 (100) Val. 3.120 (85) B
25	3.1140	3.118 (75) Val. 3.095 (10) B
2	2.8417	2.848 (8) B
3	2.7919	2.788 (40) Sen.?? 2.808 (8) B
3	2.735517	2.738 (9) Val.
3	2.700831	2.712 (9) Val.
5	2.642485	2.650 (13) Val. 2.653 (10) B
8	2.55475	2.559 (11) Sen.?? 2.559 (45) B
2	2.50915	2.511 (16) B
3	2.45701	2.456 (9) Val.
2	2.38073	2.370 (3) Val.? 2.396 (5) B 2.388 (6) B 2.377 (4) B
2	2.1934	2.204 (5) Val.? 2.196 (3) B
2	2.12917	2.146 (10) B 2.132 (10) B
3	2.06147	2.058 (9) Val. 2.063 (10) B
6	2.04629	2.046 (9) Val. 2.050 (30) B
4	1.97149	1.972 (42) Sen.?? 2.016 (5) B 1.9961 (3) 1.988 (8) B 1.972 (5) B
4	1.927224	1,9288 (11) Val.
2	1.83248	1.8356 (5) Val.
6	1.802219	1,8046 (20) Val.
4	1.79771	1.681 (35) Sen.?? 1.6745 (9) Val.
2	1.664346	1.6660 (7) Val.
2	1.639528	
1	1.608426	1.611 (11) Sen.??
3	1.568996	1.5715 (7) Val.
2	1.560577	1.562 (7) Sen.?? 1.56 (25) A
1	1.54445	1.5577 (3) Val.?
3	1.519023	1.5226 (11) Val.

*B Sb_2O_3-2SbOCl

Appendix IVD: Hydrolysis of an Oxychloride Precipitate dissolved in Hydrochloric Acid

Senarmontite plus 95%

Smear

Intensities	D-Spacing	Possible Identification
13	6.360548	6.44 (12) Sen.??
95+	3.174075	3.218 (100) Sen.
36	2.769036	2.788 (40) Sen.
10	2.545253	2.559 (11) Sen.
2	2.268493	2.276 (2) Sen.
4	2.141686	2.145 (3) Sen.
35	1.964587	1.972 (42) Sen.
2	1.881969	1.885 (2) Sen.
33	1.675593	1.681 (35) Sen.
9	1.605081	1.611 (11) Sen.
6	1.563110	1.562 (7) Sen.

Appendix IVE: Hydrolysis on Strip Solution From Solvent Extraction

Senarmontite plus 95%

Pellet

Intensities	D-Spacing	Possible Identification
67	6.403798	6.44 (12) Sen.??
95+	3.191132	3.218 (100) Sen.
44	2.783977	2.788 (40) Sen.
13	2.555346	2.559 (11) Sen.?
2	2.273113	2.276 (2) Sen.
5	2.145350	2.145 (3) Sen.
37	1.968952	1.972 (42) Sen.
2	1.882557	1.885 (2) Sen.
29	1.679305	1.681 (35) Sen.
17	1.608845	1.611 (11) Sen.
5	1.561160	1.562 (7) Sen.

Appendix IVF: Hydrolysis on Strip Solution at 40°C

senarmontite approx. 10%
valentinite approx. 72%
NH_4FeCl_3 approx. 4%

Pellet

Intensities	D-Spacing	Possible Identification
4	6.102164	6.10 (100) B?*
51	4.61043	4.571 (18) Val.
18	3.498333	3.494 (25) Val.
19	3.225827	3.174 (20) Val.? 3.218 (100 Sen.?
72	3.133169	3.142 (100) Val. 3.118 (75) Val.
4	2.793311	2.788 (40) Sen.?
5	2.745204	2.738 (9) Val.
16	2.709584	2.712 (9) Val. 2.71 (60) B?
2	2.680200	
14	2.648263	2.650 (13) Val.
13	2.459758	2.456 (9) Val.
3	2.272188	2.271 (3) Val. 2.276 (2) Sen.? 2.29 (40) B?
5	2.203735	2.204 (5) Val.
2	2.110116	2.107 (3) Val. 2.14 (20) B?
2	2.059606	2.058 (9) Val.
5	2.047397	2.046 (9) Val.
6	2.972325	1.971 (5) Val. 1.972 (42) Sen.?
8	1.931725	1.9288 (11) Val.
3	1.835629	1.8356 (5) Val.
4	1.823392	1.8178 (5) Val.
11	1.805524	1.8046 (20) Val.
8	1.679771	1.6745 (9) Val. 1.681 (35) Sen.?
4B	1.667770	1.6660 (7) Val.
3B	1.626051	1.6239 (3) Val. 1.611 (11) Sen.?
5B	1.569982	1.562 (7) Sen.
2B	1.559993	
6B	1.523218	

*B (NH_4FeCl_3) is possibly present.